

THE  
SCIENCE - HISTORY  
OF THE UNIVERSE

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VOLUME IV

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CHEMISTRY  
By WILLIAM ALLEN HAMOR

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INTRODUCTION  
By PROFESSOR CHARLES BASKERVILLE

THE  
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OF THE UNIVERSE

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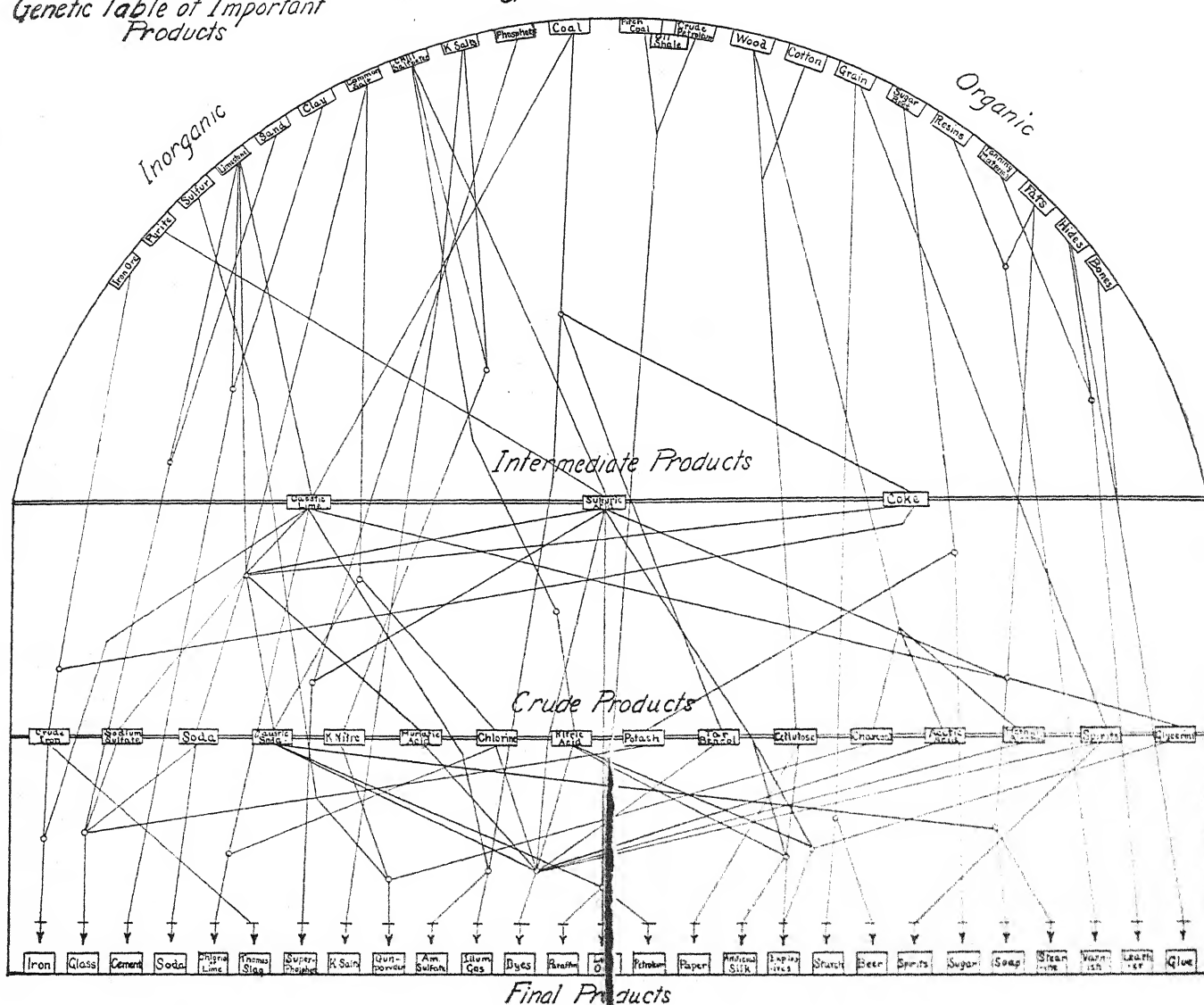
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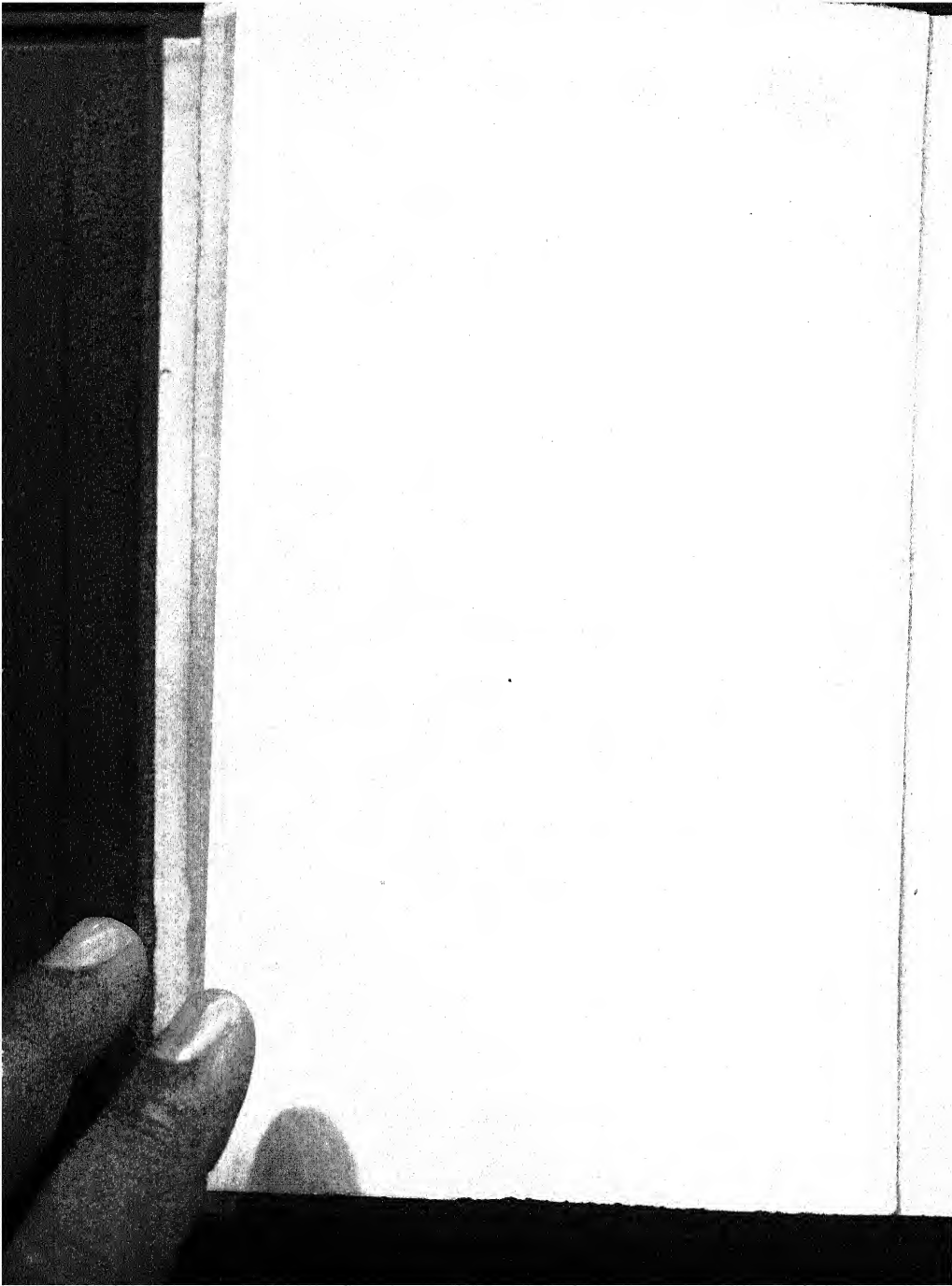
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# THE SCIENCE-HISTORY OF THE UNIVERSE

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## INTRODUCTION

TECHNICALLY it is difficult, almost impossible, to draw sharp distinctions between the various subdivisions of natural science. Omitting consideration of mathematics, which constitutes a necessary, and convenient mode of numbering, diagrammatization and quantitative interpretation of natural as well as of other phenomena—a clear and concise language—the fundamental sciences are physics and chemistry. Within the last half century the borderland of these two has become so elastic in its boundaries, that there has developed again an original science so closely involving the characteristics of the two fundamental ones that it is called physical chemistry. With a clear understanding of the foregoing there should be no misinterpretation of what follows in this “Introduction” or failure to appreciate what has been set forth within the covers of this book by its author.

Chemistry took its origin out of knowledge of small mysteries. Even today many may reasonably look with wonder at the accomplishments of the chemist, who seems to be a master at massive as well as at diminutive legerdemain. Unfortunately, at times it is assumed that he knows more than he does, and some, as in the charlatan days, pretend to be wiser than they are. The history of chemis-

try for the past two centuries has been the history of the progress of civilization. Its careful student will draw from it values that are cultural, material and moral.

Its educational value depends upon the accuracy it gives one's powers of observation, training in the correlation of the facts observed, tracing the underlying laws thus brought out, and the stimulation of the imagination to bring other facts, apparently not in conformity with the laws, into harmony with them or to so alter the explanations secured as to include the seeming exceptions. Thus theories, propounded as a logical sequence, which, as Shennstone has said, are as "searchlights which cast light into dark places and enable us to see, sometimes plainly, sometimes only in dim outline, much that would remain hidden if we were denied their aid," are scrapped like so much old metal when their usefulness ends. So the history of chemistry, like the history of inventions, "definable as a method for utilizing a discovery," often reads like a romance.

The material value of chemistry has had to do with our wealth, health and happiness. Chemistry, by the utilization of much of the wastes of the world, has produced great wealth, as is seen in the numerous dyes, synthetic medicines, etc., which have been made from coal-tar. It has also saved injurious wastes. At some of the great copper smelters to-day, where the sulphur gases were formerly turned loose into the air to the destruction of forests, they are now converted into the cheap but valuable oil of vitriol, upon the use of which there is scarcely anything we eat, drink or wear that is not directly or indirectly dependent. In fact, one may judge the financial progress of

a nation by the annual production or consumption, or both, of this acid. The industries of nations have been changed through the influence of applied chemistry. The old madder fields of France are now vineyards, the madder dye (alizarin) being made by German processes in a factory. So the millions of acres formerly given to the cultivation of the indigo plant may help feed England when they are cultivated for food products, as the Germans now manufacture a higher grade of indigo, at a lower price, than was formerly obtainable commercially from the natural sources, even with the poverty wages paid in India. Through the application of the principles of chemistry, better products have been produced at cheaper prices and thus made available for more people. Substances possessing little or no practical use, rare curiosities for the chemical museum, have become of great actual value. This may be seen in the development of incandescent gas lighting.

We have only recently come to an awakened conscience of fuel. The quantity of fuel required to produce the energy for an industrial process is dependent upon the manner in which it is required to do its work. Once smoke was regarded as an evil, then a nuisance; now it is known as a waste, and none has better cause to wage war against it than he who produces it. A smoking chimney is a thief, not only because it projects visible unburned carbon into the atmosphere, but in nine cases out of ten on account of the invisible gases which are hot and combustible. Regenerated gas heating not only prevents smoke, but is a powerful means of economizing heat. It has been estimated that the saving of national wealth effected by its universal application would amount to a sum sufficient to

pay the aggregate national debts of all the civilized nations. What a horn of plenty may be seen outlined in the dense smoke hanging like a pall over some of our cities in this country!

The problem of energy, usually expressed in terms of fuel, is a most serious one to every nation. Upon the invention of the steam engine the days of the windmill and old-time water-wheel seemed to be numbered; sailing ships gave way to mechanically driven vessels; gas-explosion engines and electric power applied to motor vehicles are driving out the horse, without whose aid at one time it was thought that no civilized nation could exist, and have given us a propelling force with which the air is navigated. In some ways there is a disposition to revert in part to the old order of things, as shown in the utilization of water power with improved appliances. Inventors are not without hope of utilizing the ocean tides; in fact, several installations where this is done do exist. The indefinite hope of some imaginative people that we may secure some unknown source of energy, however, is at present an undependable and gratuitous assumption. Therefore, it is of the utmost importance that the strictest economy be practiced in the expenditure of our fuel capital.

The conversion of the force of gravity into electrical energy by means of falling water has given an enormous impetus to progress in applied chemistry. Not only has it made the production of new and useful substances possible, as carborundum and artificial graphite, but it has cheapened the production of other materials, as caustics, "bleach," copper, aluminium, etc., in money values that involve large figures, and promises to render available bodies of metallic

ores formerly regarded worthless. Cable news tells us of the renewal of the German potash syndicate which controls the natural deposits of potash salts at Stassfurt and lays heavy tribute upon every farmer who uses mixed fertilizers. Electrical energy may yet give relief from such a tax upon every civilized person in the world, for laboratory experiments have shown the possibility of utilizing the abundant insoluble, hence unavailable, source of potash, a necessary element for plant growth, which exists in every soil, but in comparatively small, yet sufficiently large, amounts.

Perhaps the most important practical forward steps taken in applied chemistry in recent years have been along the line of the utilization of atmospheric nitrogen. No living thing, plant or animal, is known which does not contain nitrogen. Nitrogen is, therefore, necessary; it is the most expensive, yet abundant and easily wasted, element of plant food. The air contains 3,900 billion tons of this element, but it is not available, except to a limited degree, as a food. It must be properly combined with other elements for plants to feed upon it. This has recently been accomplished commercially, and its importance is realized when attention is drawn to the known sources of nitrates, and the fact is recognized that the visible supply will not suffice for the life of two generations at the normal rate of increase both in population and productivity of the soil. Fortunately, the processes devised in this day of wonderful surprises do not participate in the destruction of valuable coal deposits in obtaining the energy, but use "white coal," which, with the constant aid of nature, through the principles of evaporation and condensation, may be used over

and over again. To this end it has stimulated the efforts of many toward the conservation of the forests, for upon these depend a constant supply of water and the avoidance of devastating freshets which destroy the power plants.

The solution of problems of preventive medicine—that is, sanitation—the development of aseptic surgery, the discovery of anæsthesia, have been contributions of chemistry to human happiness. The chemist has sought and is seeking the establishment of uniform grades and international standards and agreed methods for determining them for products of exchange. Those familiar only with the secular press accounts of the struggles for pure food and drink and distinctive labels therefor realize what this means. To accomplish the refinements of this improvement in communal and international morals, however, will require a recasting of the meaning of many words in every language. This cannot fail to promote in a measure the development of a desirable universal language for all nations.

While the history of chemical economics is one of fascinating interest, it must not be forgotten that these allotments to the benefits of the living are in the end dependent upon pure chemistry. In most cases they have resulted from the application of principles derived from facts which presented no utilitarian aspect in themselves, and the principles, too, appeared to have only the remotest connection with utility. It is not intended to imply that applied chemistry has been or is entirely dependent upon pure chemistry, for there are numerous instances where what knowledge we possess in the speculative and real field of the science has received its initial impulse from some useful application.

The progress of the science has often been with a halting step. Three important misconceptions—namely, the immaterial nature of gases, the inverted notion of combustion and the material nature of heat—had first to be removed before the idea that matter is composed not only of molecules but of atoms, could gain acceptance in the beginning of the nineteenth century. By the atomic conception of Dalton (1803) different kinds of matter are dependent not only upon different kinds of molecules, but different kinds of atoms in molecules, and, furthermore, as later proved, even the configuration of the atoms within the molecules.

Various energy demonstrations, as heat, electricity and light, bring about various changes in these molecules to produce different kinds of matter. We know carbon dioxide and water, under conditions which obtain in the leaf of a tree, under the influence of light combine with the elimination of oxygen and the production of sugar. The chemist as an expert achievement can produce sugar in his laboratory, but so far he has little understanding of the chemical action of light in the laboratory of the leaf. Altho photochemistry promises soon to yield results which may not be devoid of startling interest, we do not know how nature does many things that we are accustomed to see around us and attribute to a so-called vital force. In exercising the utmost care to avoid confusing the accomplished with the projected, the thesis may be reverently supported that life is energy or a manifestation thereof.

One were devoid of judgment did he not let it be clearly understood that he appreciates the objections, such as retention of form through years, reproduction of species and atavistic inheritance of character, that may be raised with

reason in opposition to the mechanical, physical, chemical or energy explanation of life. As yet we do not know the constitution of the highly complicated structures of the carbon, hydrogen, oxygen, nitrogen and sulphur compounds of the nucleus—"chemical matter," as Neumeister says. The same could have been truly said of the sugars before Fischer's masterly work, beginning about a generation ago, or Osborne's more recent work upon the nucleins of wheat. Can we say, having learned the structure and synthesized the nucleus, that we shall not be able in the laboratory to give it that impulse which launches it upon a career of reproduction?

Our militant egoism need not be shocked by apparently

Nourishing a youth sublime  
With the fairy tales of science.

We thought we knew the air, but within the last two decades it has been learned that the atmosphere contains 1 per cent. of an element never dreamed of—namely, argon. We thought every chemical atom was characterized by a distinct ability to combine with other atoms to form compounds. Argon and four other similar elements, including helium, since found, are devoid of this characteristic.

The nineteenth century gave us Crookes' tubes, which made the discovery of Röntgen rays possible and gave the hint that established the existence of the Becquerel rays, the pursuit of which eventuated in the unmasking of radium by the Curies. This remarkable substance carries enormous charges of readily detectable energy and under certain conditions changes into another element, helium (Ramsay and Soddy). The transmutation of the elements has been experimentally demonstrated. In such considerations confusion of terms must be studiously avoided. Philosophically, radium cannot be an element, because its molecule breaks up into something other than an atom of the same thing, yet it has a recognized place in the



table of elements. This latter fact is due to an agreement among chemists to recognize a substance as an element which, under proper conditions, exhibits a spectrum showing characteristic lines possessed by no other element and possesses a definite combining weight. Radium satisfies these two requirements and constitutes an exception to the general proposition of consistency of atoms in an elementary molecule. If we retain the term element, and there is no indication of its being discarded soon, its definition must be broadened.

A philosophic idea has come forward at intervals ever since the days when we have written records of men's thoughts—namely, that there is, or was, one, the simplest substance of which all matter is, or was, made. If that be true—and perhaps it is—then we only require the knowledge of how to change one element into another and the necessary apparatus to make the idea an accomplished fact. So far, however, we have observed only the disintegration of the elements and we must yet build them up.

A knowledge of the cathode rays produced within a Crookes tube gave J. J. Thomson and Rutherford experimental data for the latest interpretations of the phenomena of radio-activity and the most modern answer to the question of "What is matter?"

Thirty years ago Crookes suggested the existence of an ultra-gaseous state of matter, a protyle, of which all matter is composed, and that its particle weighs about one-thousandth that of a hydrogen atom, the lightest atom known. Thomson, following an elaborate procedure, weighed these particles and found that the value was between 800 and 1,000. As they bear electric charges, he designated them electrons. Rutherford has shown that in the disintegration of radium a gas, called emanation, is produced. This, in turn, changes through several steps and continuously into helium. The change consists in hurling particles, called  $\alpha$ -particles, at a terrific speed from the emanation. These particles are atoms of helium plus an electron, which is lost

in time. By weighing before and after, the weight of the electron is determined. These values coincide with those obtained by Thomson. Etymologically, an atom means something which cannot be divided. We have been accustomed to apply the term to that chemical individual which has not yet been divided. As soon as it is shown to be complex the particle ceases to be an atom. As language changes there can be little objection, if it is done by common agreement so there may be no misunderstanding, to applying the term electron to a real atom or the real indivisible particle, for undoubtedly the atom of Dalton is complex.

Therefore, matter is composed of molecules. Molecules are made up of atoms. Atoms consist of electrons. Electrons are charges of electricity. But what is electricity? Ostwald asserts that we are aware of matter only through the evidences of energy. Matter is an assemblage of energy systems; there is no matter. All resolves itself into the mechanics of energy. Heat, electricity and life are elementary energy systems, having definite capacity and intensity, and as chemical entities with their equivalents, represent our atomic conceptions. But here we go into the realm of metaphysics. Many of the secrets of nature have been gained, laboriously wrought for, but rich rewards await the coming generations who inherit a knowledge of the extremities of our globe but must yet learn of its interior.

Science may therefore be looked upon as a gem, beautifully cut, with its many facets. We view the light from one face, or more, with the play of colors most exquisite to the eye and gratifying to the senses. Whence the light? That is nature, the throbbing pulsation of which, controlled by some All-great, hence All-wise, Providence, makes our universe what it is, however little or much of it we may or may not comprehend.

CHARLES BASKERVILLE.

# CHEMISTRY

## CHAPTER I

### DEVELOPMENT OF THE CHEMICAL CONCEPTION

TO MANY intelligent and cultivated persons not specifically instructed in Chemistry, this word recalls confused memories of colored liquids, glistening crystals, dazzling flames, suffocating fumes, intolerable odors, startling explosions and a chaos of mystifying experiments, the interest in which is proportional to the danger supposed to attend their exhibition. Further reminiscences are of many singular objects in wood, metal, glass and earthenware; of retorts and condensers, furnaces and crucibles, together with bottles innumerable filled with solids, liquids and gases. This whole bewildering paraphernalia, moreover, is connected by glass tubes of eccentric curves, displayed in inextricable confusion and meaningless array.

Behind this chaos arise vague memories of a professor or teacher discoursing learnedly in a polysyllabic jargon, and attempting to explain the unusual phenomena in words which seemed stranger than the experiments themselves. It is rarely forgotten, as H. C. Bolton suggests, how potent was the fascination exerted upon the hearer, a feeling of awe and mystery as tho the mind were approaching the border of the supernatural, impressions that have clung to chemistry ever since its entanglement with the superstitions of alchemy, astrology and the "black art."

Men and women interested in modern thought who

undertake to gain through chemical literature a knowledge of what chemists are doing in and for the world encounter a discouraging nomenclature which repels them by its apparent intricacy and cumbrousness. Their opinion of the terminology of an exact science is not enhanced when they learn that "black lead" contains no lead, "copperas" no copper, "mosaic gold" no gold, and "German silver" no silver; that "carbolic acid" is not an acid, "oil of vitriol" is not an oil; that some sugars and some kinds of wax are alcohols; that "cream of tartar" has nothing in common with cream, "milk of lime" with milk, "butter of antimony" with butter, "sugar of lead" with sugar, nor "liver of sulphur" with the animal organ from which it was named.

Readers of chemical writings sometimes fail to appreciate the advantages of styling borax "di-meta-borate of sodium," or of calling common alcohol "methyl hydrate," and they ignore the euphony in such words as pentamethyldiamidodithiodiphenylamindiodomethylate (a substance baptized by Dr. Albert Maasen).

Those whose chemical education consisted in attendance on a course of lectures illustrated by experiments performed in their presence, interspersed with occasional recitations from a prosaic text-book which taxed the memory in true Chinese fashion, may be pardoned for retaining very hazy impressions of the true character of the science. On the other hand, many thinking and reading persons recognize the magnitude of the scope and operations of chemistry, and have some appreciation of its benefits to mankind. It is not to be unexpected, however, that the layman's conception of chemistry in the abstract—the cold, exact, abstruse science—seems as far removed from the realms of romance as the higher mathematics. Yet mathematics and music are strangely correlated; and so it is not to be wondered at that the chemist himself, the enthusiastic master of mysteries, finds in his modern

miracle making that proportion of romanticism necessary, perhaps, to the mental well-being of the individual.

The widely varying ideas which have prevailed at different periods in the history of chemical science, with regard to its nature and object, are significantly portrayed in the definitions of chemistry which have obtained at these periods, and an examination of the following collection of definitions will reveal a curious growth:

*Old Proverb.* "Alchimia est ars, cujus initium laborare, medium mentiri, finis mendicare." Alchemy is an art, the beginning of which is to work, the middle to lie, the end to beg.

*Suidas* (a Greek lexicographer of the eleventh century). "Chemistry, the artificial preparation of silver and gold."

*Paracelsus* (1537 [?]). "Chemistry is the art of resolving bodies."

*Denis Lachaire* (1540 [?]). "Chemistry (alchemy) is that part of natural philosophy which teaches the preparation of metals on the earth by imitating the operations of Nature in the earth as closely as possible."

*Van Helmont* (1620 [?]). "Chemistry is the art of analyzing bodies by fire."

*A Chymical Dictionary*, London, 1650. "Chimia is the art of separating pure from impure and of making essences."

*Salmon* (1672). "Chemistry is an art or a practical science which teaches the methods of resolving compound bodies into their natural principles, and by this means rendering them most pure and most efficacious as a medicine, either for curing diseases or for perfecting the imperfect metals." ("Bibliothèque des Philosophes Chimiques," Paris, 1672.)

*Lemery* (1675). "Chemistry is the art which teaches the methods of separating the different sub-

stances contained in a compound." ("Cours de Chymie," Paris, 1675.)

*Boerhaave* (1724). "Chemistry is an art whereby sensible bodies contained in vessels (or at least capable of being contained therein and rendered sensible) are so changed by means of certain instruments, and especially fire, that their several powers and virtues are thereby discovered with a view to the uses of medicine, natural philosophy and other arts, and occasion of life." ("Elementa Chymiae," 1724.)

*Pernety* (1758). "Common chemistry (*chimie vulgaire*) is the art of destroying the compounds which Nature has made. Hermetic chemistry is the art of assisting Nature to perfect them." ("Fables Egyptiennes et Grecques," Paris, 1766.)

*Pernety* (1787). "Alchemy is a science and the art of making a fermenting powder which serves as a universal remedy for all the diseases of men, animals, and plants.

"*Dictionnaire Mytho-hermetique*," Paris (1787). "False alchemy cannot better be defined than the act of making one's self miserable, both as regards fortune and health."

*Nicholson* (1795). "Chemistry as a science teaches the methods of estimating and accounting for the changes produced in bodies by motions of their parts amongst each other which are too minute to affect the senses individually; and as an art it consists in the application of bodies to each other in such situations as are best calculated to produce those changes." ("Dictionary of Chemistry," London, 1795.)

*H. Davy* (1802). "Chemistry is that part of natural philosophy which relates to those intimate actions of bodies upon each other, by which their appearances are altered and their individuality destroyed." ("Lectures" in *Collected Works*, vol. ii, 1839.)

*Thomson* (1810). "The object of chemistry is to

ascertain the ingredients of which bodies are composed; to examine the compounds formed by the combination of those ingredients; and to investigate the nature of the power which occasions these combinations." ("System of Chemistry," 1819.)

*Frankland* (1866). "Chemistry is the science which treats of the atomic composition of bodies and of those changes in matter which result from an alteration in the relative position of atoms." ("Lecture Notes for Students," London, 1866.)

*Rodwell* (1873). "Chemistry is the science which treats of the various kinds of matter, whether simple or compound, their properties and the laws which govern their combination with and separation from each other." ("Birth of Chemistry," London, 1873.)

*Roscoe* (1873). "The science of chemistry has for its aim the experimental examination of the properties of the elements and their compounds, and the investigation of the laws which regulate their combination one with another."

*Ostwald* (1890). "Chemistry is the science which treats of the different forms of matter, their properties, and the changes which they undergo."

*Mendeleeff* (1891). "Chemistry is concerned with the study of the homogeneous substances or material of which all the objects of the universe are made up, with the transformations of these substances into each other, and with the phenomena which accompany such transformations."

*Remsen* (1892). "The science of chemistry has to deal with everything connected with the deepest-seated changes in composition which the different forms of matter undergo."

At the present time, chemistry is usually defined as the study of matter and the changes produced in it by the action of chemical force or other forms of energy upon it. It rests upon a secure basis of fact, and its first object

consists in learning the constituents of which the material world is composed, in reducing these constituents to their simplest forms, and in building up new chemical compounds from the latter. These problems, along with the task of determining the laws governing the chemical combination of matter, occupy the time and thought of the chemists of the present day.

The Egyptians, Hebrews, Phœnicians and other ancients acquired a certain indefinite knowledge of chemical processes in a purely accidental manner, which were applied for the practical results obtainable, but no explanation of these processes was deduced. Neither did the Greeks and Romans make any attempts to collate facts then known or to pursue the investigation of natural phenomena for the attainment of a definite purpose, nor before the fourth century of the present era were endeavors made to gain an insight into chemical processes by experiment. Such a lack of data did not prevent the peoples of antiquity from speculating on the nature of matter, however, and their views upon the ultimate constituents, or "elements," of the organized world have given the first age of chemistry a characterizing feature.

Altho there is no positive evidence that the Greeks and Romans were acquainted with a belief in the production of precious metals from base metals, yet the theory that one element can be transformed into another was developed from the ancient doctrines of the nature of the elements, and at the beginning of the present era, primarily in Egypt, attempts were made to transform the base metals into gold and silver. The art of transmutation was termed 'chemia,' a word which is probably derived from the North Egyptian name for Egypt (von Meyer). This term is mentioned by Plutarch as the name of Egypt, but there is some diversity among etymologists whether the present word 'chemistry' is derived from this Egyptian word; the Arabic 'kema,' meaning secreting; the Sanskrit 'kema,' meaning gold; or the Greek 'chymos,' meaning fluid.



Alchemy, which is derived from the Arabic 'al-kimiya,' an agent for effecting transmutation, had for its object the solution of the problem of transmutation, the attainment of the so-called "philosopher's stone," by the aid of which metals were to be transmuted and the life of man prolonged. This task characterized the Age of Alchemy, a period extending for at least twelve centuries. This age was one of magic and necromancy, but effected the extension of the knowledge of chemical facts.

The next period in the history of chemistry is known as the Iatro-Chemical, or the period of medical mysticism. This period extended from the first half of the sixteenth century to the middle of the seventeenth century and was characterized by the absorption of medicine by chemistry. However, chemistry did not lose its alchemistic tendencies and was not yet an independent branch of natural science.

After the Iatro-Chemical Period occurred a transition period and chemistry became a science. This period is known as the period of the Phlogiston Theory, owing to the fact that the chemists at the end of the seventeenth and during most of the eighteenth century attempted to explain the phenomena of combustion by assuming the existence of a hypothetical principle of combustibility, 'phlogiston.'

The early part of the most recent period in the history of chemistry is characterized by the decline and fall of the phlogiston theory and its replacement by the anti-phlogistic chemistry of Lavoisier, which laid the foundation of the new chemistry, a science which covers the era of quantitative investigation. This era has had for its guiding star the chemical atomic theory, and the immense strides made in the science during the latest epoch are due to the exact study of chemical composition and the close investigation of physico-chemical relations.

terial nature, ether. In the Laws of Menu the subtle ether is spoken of as being the first created, and from this, by transmutation, came air, and this through some change became light or fire, and by a further change in this came water, from which lastly earth is deposited. This theory was accepted by the Brahmans and Buddhists and found its way into Europe. In the 'Anguttara Nikaja' consciousness is named as a sixth element, and in the writings of Kapila, the leading exponent of the Samkhya philosophy, it is stated that there are five subtle particles, rudiments or atoms—perceptible to beings of a superior order but unapprehended by the grosser senses of mankind—derived from the conscious principle and themselves productive of the five grosser elements, earth, water, fire, air and space. Kanada, who founded the Nyaya system of philosophy, proposed an atomic theory in which he states that atoms are eternal and that the ultimate atom is simple.

One of the oldest of the Chinese classics, the 'Shu King,' contains a document of still greater antiquity termed "The Great Plan with Its Nine Divisions," the first division of which speaks of water, fire, wood, metal and earth as the elementary substances which went to build up the universe. This document probably depicts a belief five thousand years old and it is known that the above mentioned substances were regarded as elements in the dynasty of Hoang-Ti (2698-2599 B.C.). In that most obscure Chinese classic, the 'Yi King,' fire and water, wind and thunder, the ocean and the mountains, appear to be recognised as the elements.

The most complete theories of the ultimate constituents of bodies have come down from the Greeks, although it is highly probable that the Greek philosophers did not themselves deduce their theories of atoms and elements, but derived them from other sources. Some have maintained that the Pythagorean theories are derived from the philosophy of the Chinese; but, since the Greeks came from Asia as did the other Indo-Germanic races, it is natural to

suppose that they brought various Eastern theories with them, modified them according to their environment and developed them by their own powers.

The earliest Greek cosmogonists were those of the Ionic school, which was founded by Thales of Miletus, who lived about 600 B.C. Thales considered that water was the material cause of all things, and was ignorant of the atmosphere or air. Such views, as well as those of Anaximenes and Heraclitus (in the sixth century B.C.), who ascribed to air and fire respectively the rôle of ground material, have had no influence upon the development of chemical knowledge.

Leucippus, who lived in the fifth century B.C. and who is regarded as the founder of the Atomistic school, considered that all things consisted of spaces and atoms, the latter being further indivisible, having only quantitative differences between one another and being always in motion. This theory was further developed by Democritus of Abdera, who took a primal element as the basis of his speculations, but subdivided this further in that he imagined it to be made up of atoms, which differed from one another in form and size, but not in the nature of their substance. According to him, all the changes in the world consisted in the separation and recombination of these atoms.

Empedocles of Agrigent (500 B.C.) regarded the 'elements' air, water, earth and fire as the basis of the world, and maintained the constancy of matter. He did not speak of the derivation of the elements from a single substratum or of ultimate atoms, and in his system the contending forces cause the combination and separation of the elements.

The system of natural philosophy of Plato (427-344 B.C.) has been practically without influence on the development of physical science. Plato assumed the existence of the four elements of Empedocles and propounded mathematical doctrines concerning these elements, but disregarded cer-

tain difficulties pointed out by subsequent philosophers. His pupil, Aristotle (384-322 B.C.), however, among the most famous of the Greek philosophers, is deemed the



Fig. 1 —DEMOCRITUS OF ABDERA (450 B.C.), WHO TAUGHT AN ATOMIC THEORY.

sage who exercised the most influence upon subsequent thought. Aristotle considered that four elements were insufficient in themselves to explain the phenomena of Nature; he therefore assumed a fifth one, which he imag-

ined to have an ethereal nature and to permeate the universe.

The followers of the Aristotelian doctrine in the Middle Ages supposed this 'element' to be material, the 'quinta essentia,' and made many endeavors to isolate it, causing endless confusion. The Stagirite considered the properties of bodies to be the result of the simultaneous occurrence and intermingling of fundamental conditions, and regarded



Fig. 2 —ARISTOTLE AND HIS STUDENTS.

the component elements only in the sense of bearers of these fundamental properties. He held that the chief qualities of the elements were those apparent to the touch, as warm, cold, dry and moist, and maintained that each of the elements of Empedocles is characterized by the possession of two of these fundamental properties, air being warm and moist, water moist and cold, earth cold and dry, and fire dry and warm. He concluded, therefore, that the differences in the material world were to be attributed to

the properties inherent in matter and that the elements can change one into another.

In Aristotle's opinion, the transmutation of the elements happens owing to the abstraction of certain qualities and the substitution of others; hence, he concluded that an element can more readily change into one with which it has one quality in common, as cold water to cold earth and hot fire to hot air, than into one completely its opposite, as hot, dry fire to cold, wet water. Aristotle regarded the change of water into steam as a transmutation of the elements, a qualitative change of material, as otherwise he could not explain the great change of bulk if the steam had previously existed in the water without change or difference. Views of this nature on the states of the aggregation of matter led to the idea of transforming one kind of matter into another, and the generalization of the Aristotelian ideas fostered the belief in the possibility of the transmutation of metals, a particular feature of the alchemistic period.

It is unnecessary to point out how widely the above mentioned views with regard to the elements deviate from the conceptions of modern chemistry, yet the Greek philosophers, with the freedom and boldness of the Hellenic mind, and an ability to infer and enunciate, had grasped the idea of elemental substances, elements out of which all things were made—the principles of things—and had thought out the existence of atoms as the ultimate constituents of matter. The belief in the existence of the Hindu and Aristotelian element ether was and still is assumed as a necessity for explaining many phenomena. Various chemical facts had been learned by empirical methods and by accident, but the Greeks overvalued the deductive and undervalued the inductive method, and held aloof from the observation and practice of chemical processes.

In the earliest records of the Egyptians, Jews and Hindus there is to be found an acquaintance with the working of different metals, which art was held by the younger of

those nations to have been taught by mythical personages. On reference to the drawings found on the tombs in Egypt, figures are shown therein illustrating the art of metallurgy, and it has been learned that the operations were conducted by weighed portions of matter. Moreover, Biblical history records that the Jews were acquainted with gold, silver, copper, iron, and probably lead and tin, and that a form of balance was used for weighing metal. The Greeks and Romans were familiar with many metallurgical processes, but made no attempts to explain the chemical processes involved in the smelting of ores.

The ancients believed that the metals were produced by the penetration of air into the vitals of the earth, and assumed that the amount of metal increased as the mine proceeded inward. This conception was based on the testimony of Aristotle and was entertained for a long time.

Gold and silver were the metals earliest known and were valued highly in the early times. The gold mines of Nubia were worked by the Egyptians, and in the time of Rameses II. these mines yielded gold to the value of \$600,000,000 per annum. The Phoenicians obtained gold in Eastern Africa and were the first to mine gold on the Island of Thasos. The malleability of gold rendered it possible for the ancients to gild objects by covering them with thin sheets of the metal, and they later learned to produce a layer of gold on objects by dissolving the metal in mercury and heating the amalgam produced. The older nations were acquainted with processes for freeing gold from admixtures, as there are extant records of purifying gold dust by melting it with lead and salt for some time, a method practiced at a very early period and referred to in various parts of Scripture. Pliny describes the purification of gold by means of mercury, and the process used in his time was similar to the amalgamation process practiced at the present day. In general it may be stated that the old and new methods of obtaining gold differ in details not in principle.

Silver was supplied to the ancients by the Phoenicians,



who worked the Rio Tinto mines in Spain, the native silver mines of Laurium, and the mines in Armenia. According to Posidonius, silver was discovered in Spain by the forests taking fire and melting some of the ore in which the precious metal was imbedded. Strabo states that silver was purified by fusion with lead, but it does not appear that the separation of silver from gold was known before the present era. Beckmann states that the ancients used an alloy of gold and silver, afterward termed 'electrum,' because they were unacquainted with the art of separating these metals, and it is known that an amalgam of gold and

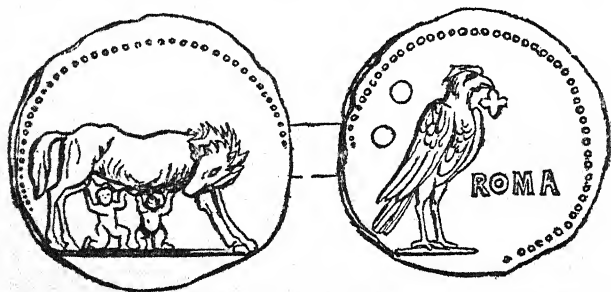


Fig. 3 —ANCIENT GOLD MEDAL, COMMEMORATING THE FOUNDATION OF ROME.

silver was regarded in ancient times as an individual metal, being termed 'asm' by the Egyptians.

Copper has been known from the earliest times, and some authorities consider that it was the next metal after gold which man learned to extract and reduce. The present state of archeological research does not suffice to locate all the principal copper mines of the ancients nor to compute the quantity of metal which they yielded, but it is believed that both the Hindus and Chinese made coins of this metal at a period which may be fixed approximately at about three thousand years ago. Copper was one of the greatest articles of commerce with the Phenicians, who de-



rived a large supply from the mines of Nubia, which at one time supplied the whole of the western world. They combined with it the tin obtained from the islands of Cyprus and Britain to make the bronze of commerce, which was early used for making weapons, ornaments and utensils; and



Fig. 4 —CARTHAGINIAN SHIELD, PLATED WITH SILVER.

the ancient civilized nations were acquainted with bronze before they had learned to prepare tin in a metallic state. Palmer states that it is evident that the copper mines in the neighborhood of Serabit el Khadim and Magharah, in Egypt, were in full working order at the time of the Exodus; and Bauerman is authority for the statement that

the period over which the working of the copper mines at Wady Magharah extends, according to hieroglyphic evidence, is from the third to the thirteenth Manethonian dynasties. With regard to the smelting processes by which the 'aes,' or copper, of the ancients was obtained, nothing certain has as yet been ascertained.

The concurrent testimonies of Hindu, Assyrian, Babylonian and Greek tradition, as well as its own etymology, fix the discovery of iron—that is to say, the invention of smelting iron ore and of manufacturing iron and steel, or the escape of the invention from the temples—at a period not earlier than the fifteenth century B.C. Among others, Brahma, Krishna, Nin-Ies, Jason and Osiris were credited with the invention of iron. Lepsius is authority for the statement that iron has been in use in Egypt for more than five thousand years, and it is well known that the Egyptians early learnt to temper iron, which they employed for the manufacture of a variety of hard instruments.

Kirchmaier, a writer of the seventeenth century, hazarded the conjecture that Adam was the first to use iron for economic purposes, to which opinion there are no satisfactory objections based on evidence. The ancients prepared iron from brown iron ore and magnetite in smelting furnaces, but no particulars are vouchsafed as to the actual process used. However, old Roman iron smelting furnaces have recently been uncarthed near Eisenberg in the Pfalz, and the form of furnace used by the Egyptians may be judged from various inscriptions.

Lead was used by the Romans for making water pipes, writing tables and coins, and soldering with lead or with an alloy of lead and tin was also well known. The Romans worked the lead ore deposits of Britain, but little is known with regard to the smelting processes used. Tin was prepared quite pure in olden times and was used in the preparation of two important alloys, solder and bronze. The Phenicians obtained tin either from India or Britain and the Israelites procured some from the Midianites. Among

the Romans lead and tin were distinguished from one another as 'plumbum nigrum' and 'plumbum candidum.' 'Stannum,' the present Latin word for tin, signified an alloy of tin and lead.

Brass, an alloy of zinc and copper, was first described by Aristotle and was long regarded as copper which had been colored yellow by fusing it with 'cadmia,' an ore of zinc often mentioned in ancient writings as having been found in Cyprus, but was not recognized as an alloy to a much later date, and zinc as an individual metal was not known to the ancients. The name 'cadmia' is said to have been derived from Cadmus, who is reputed to have introduced the making of brass at Thebes, but this is doubtless incorrect. 'Cadmia' was also used as a medicine as early as 300 B.C.

When the metal mercury, or quicksilver, was first discovered is not known, but its preparation from cinnabar by means of copper and vinegar is mentioned by Theophrastus (about 300 B.C.) and it was known at least as early as Aristotle's time. Some writers consider that in the passage in the Bible where Moses directs that all the metals taken from the Amalekites should be made to pass through the fire and afterward to be "purified by the water of separation," that this "water of separation" was mercury, but this is not based on fact.

Dioscorides describes the production of mercury from cinnabar and iron, and Pliny refers to the purification of mercury by forcing it through leather. The ancients were aware of the fact that mercury "attracts particles of gold and unites with them," and Vitruvius describes the manner of recovering gold from cloth in which it has been woven by this means. The principal ore of mercury, cinnabar, mercuric sulphide, would not fail to attract the attention of the crudest folk by its brilliant red color, and there are sufficient evidences to show that it was used as a pigment or paint by the Romans, Ethiopians and Jews.

Glass, the transparent solid formed by the fusion of

siliceous and alkaline matter, was known to the Phenicians and constituted for a long time an important manufacture of that people, because of its ingredients—natron, sand and fuel—abounding upon their coasts. The art of making glass, however, originated in China and Egypt, and its discovery in the last mentioned country was accidental, soda having been added as a flux to sand containing gold for the purpose of extracting the latter. Glass ornaments have been discovered in Egyptian tombs which are as old as the days of Moses, and Pliny and Strabo give accounts of the famous glass works of Sidon and Alexandria. The Greeks acquired the art of glass making in the fifth century B.C., and the Romans used glass for windows, mirrors and various other purposes. Rawlinson states that transparent glass was brought into use, or at least the oldest specimen found is, in the reign of Sargon II., 710 B.C.

The artificial coloring of glass by metallic oxides was discovered at a very early date, and remains have been found in ancient Egypt which indicate that methods for producing enamels and artificial gems were known. Ancient profane authors make mention of immense emeralds which are considered now to have been made of glass, and Pliny states that beryl, opal, sapphire, amethyst, etc., could be imitated, but that these imitations were softer and lighter than the real gems. The art of engraving on glass was also known in ancient times and the ancient Assyrians cut gems with great skill.

The art of pottery presents a more ancient and closer alliance between art and utility than any other branch of manufacture, and the date at which this art began to show itself is lost in the darkness of remote antiquity. The old Egyptians understood how to coat their earthen vessels with colored enamel, and porcelain was discovered and employed by the Chinese at an early date. The potter's wheel is probably the most ancient mechanical appliance which industrial art has invented.

The people of ancient times prepared soap by the action

of alkalis on fats, and drew a distinction between soft and hard soaps, according as potash or soda was used in the manufacture. According to Pliny, the soap in Germany and Gaul was prepared from animal fat and a water extract of plant ashes strengthened by adding lime.

The art of dyeing no doubt originated in that love of distinction inherent in the human mind, inducing man, for its gratification, to stain his dress or his skin with the gaudy colors of the vegetable kingdom, and was practiced very long before any views were entertained as to the nature of the changes which occurred in the chemical processes involved. The Egyptians developed dyeing with some degree of scientific precision, as they were acquainted with the use of mordants, learning that alum imparted no color itself but fixed certain dyes on cloth, and perfected the dyeing of purple.

Tyre made dyeing one of its principal occupations, and it has been asserted that the invention of the celebrated dye, Tyrian purple, was made in that city. The discovery of this purple dye is said to have been made 1,500 years before the Christian era, and Pliny states that the juice for communicating it was obtained from two different kinds of shell-fish. Kermes, indigo, madder, archil, safflower, alkanet, henna, broom, galls, walnut, pomegranate seeds, Egyptian acacia and litmus were used as coloring matter in the ancient times. In Pliny's time, white lead, cinnabar, vermilion, smalt, verdigris, hematite, soot and indigo blue were used for painting, and ink was prepared by mixing soot with gum. Galena (sulphide of lead) and realgar and orpiment (sulphides of arsenic) were used for pigments and medicines, notwithstanding the fact that their poisonous action was known.

The Egyptians were the first to use chemical preparations for medicinal purposes. Verdigris, white lead, litharge, alum, soda and niter were employed in making medicaments, and lead plasters were made from litharge and oil. Iron rust was a very old medicine; and Homer

speaks of sulphur being burnt to expel the evil spirits from a home. It was also used for purifying clothes, conserving wine and for destroying foul odors.

Among other substances whose application dates from a very early period may be mentioned lime, which was burnt and used in making mortar, and for causticizing soda for soap making; soda and potash, which were used in washing, glass making and soap making; bitumen and asphalt, which were employed for cements, torches and embalming; and acetic acid in the form of crude wine vinegar, which the ancients assumed as being present in all acid plant juices and considered to be a powerful solvent. Among the other organic compounds known at the beginning of the Christian era and possibly before then, were sugar, starch, petroleum, oil of turpentine, and various fatty and ethereal oils. Sugar was obtained from the sugar cane, starch from wheat, and the fatty oils (olive, almond and castor oils) were pressed from seeds and fruits. Oil of turpentine was prepared by distilling pine resin. The ancients were familiar with beer, wine and bread making, but did not, with their disinclination toward observation, know that alcohol and a gas different from air (carbonic acid) are formed during such processes of fermentation.

The fact that wine yielded an inflammable substance was noted by Aristotle however; but this body was not isolated.

The most ancient Latin treatises on chemical technology are the 'Compositiones ad Tingenda,' dating from the close of the eighth century and the 'Mappæ Clavicula,' written before the tenth century. In the first-mentioned work, a very rational grouping of substances occurs; the minerals and earths are by themselves; then follow gums, resins, and other products of plants; and thirdly, substances derived from the ocean.

## CHAPTER III

### THE EARLY ALCHEMISTS

THE origin of alchemy undoubtedly is to be sought for in remote antiquity, as mythical tradition reveals the sources from which the belief in the transmutation of metals was nourished, and the primary historical sources are rare and obscure. However, it appears that alchemy was pursued as a secret science, held in honor, among the Egyptians, Chaldeans and other nations.

The almost universal tradition among alchemists is that their art was first cultivated among the Egyptians; and when it is recalled that ancient Egypt was a country where the chemical art was widely practiced, it is not surprising that the earliest records of alchemy are to be found there. Clement of Alexandria states that the knowledge of the art was confined to the priests, who were prohibited to communicate it to any but the heir-apparent to the throne and to such among the priestly caste as were virtuous and wise; and Plutarch mentions that the strictest secrecy was observed. It would seem that the art of alchemy was especially cultivated at Memphis, and Ptah-mer, the high priest of Memphis, was so great an adept that he was said to be familiar with all things.

The first dominant personality with which the origin of alchemy is associated is that of Hermes Trismegistus, and the alchemists acknowledge him as one of the earliest masters, if not the originator of their creed and craft. This Hermes, some assert, is identical with Canaan, the



son of Ham, and the name is synonymous with the old Egyptian godhead Thoth, which, when endowed with the serpent-staff as the symbol of wisdom, was compared by the Grecians with their Hermes. Hermes Trismegistus was said to be the author of twenty thousand or more books, which probably indicates that, as the god of letters, all books were dedicated to him, and in Roman Egypt pillars were erected in his honor, upon which alchemistic inscriptions were put in the form of hieroglyphics.

In the eleventh century the alchemist Hortulanus announced the Latin version of an essay which he ascribed to Hermes. This came to be known as the "Smaragdine Table," or "Tabula Smaragdina," and it is probably one of the earliest of the Hermetic philosophical or alchemistic writings. An English translation of this essay is as follows:

"True it is without a lie, sure and most true; what is below is like that which is above. And what is above is like that which is below, of one substance to perform miracles.

"And as all things have come from one being, the meditation of one, so all things have been generated from this one thing by adoption.

"Its father is the sun, its mother is the moon. The wind has carried it in its womb. Its nurse is the earth. The father of every talisman of the whole world is this. Its power is unimpaired when it is turned upon the earth.

"Separate the earth from the fire, the subtile from the material, gently, with great cleverness. It rises from the earth to heaven and again descends upon earth, and receives the force of those above and those below.

"Thus thou wilt have the glory of the whole world. All obscurity, therefore, will leave thee.

"This is of all strength the strong strength, because



it will subdue every subtle thing and penetrate every solid.

"Thus has the world been created. Hence there will be wonderful adoptions whose measure is this.

"Therefore I have been called Hermes Trismegistos, possessing three parts of the philosophy of the whole world.

"What I have said of the operation of the sun has been fulfilled."

This essay is obscure enough to receive almost any interpretation.

The Chaldeans, who were masters of occult sciences, undertook the fusion of astrology and magic, and the belief in the connection between the sun and planets and the metals, which was assumed for a long period, was of Babylonian origin. It was believed that the planets influenced a growth of the metals, and the signs of the heavenly bodies became the symbols of the metals; in fact, the metals were called by the names of the stars up to the end of the eighteenth century. One writer of the fifth century A.D. states that gold corresponds to the sun, silver to the moon, lead to Saturn, tin to Mercury, iron to Mars, and copper to Venus.

In the thirteenth century symbols were used freely to denote some of the metals; as, for example, gold, Sol, was represented by a circle with a dot in its center; silver, Luna, was depicted by a crescent; and copper, Venus, was denoted by the symbol used by Glauber at a later date. Many of the alchemists saw in these symbols an indication of the metals they represented. Thus the circle illustrated perfection of the metallic condition, while the semi-circle indicated only an approximation to this state. Some have supposed that the symbol for copper, Venus, represented a hand mirror, and this is highly probable.

The Jews, who were believers in magic, played an important part in the fusion of eastern and western doctrine at the time of the birth of Christianity, and some

writings on alchemy have been ascribed to Jewish writers. The later alchemists recorded various Biblical characters as alchemists on the authority of the Bible, as Adam, Tubal-Cain, Moses and his sister Miriam, and John; and referred the origin of alchemy to the time before the flood.



Sun,  
Gold.



Moon,  
Silver.



Mercury  
Quicksilver.



Venus,  
Copper.



Mars,  
Iron.



Saturn,  
Lead.



Jupiter,  
Tin.



Fig. 5 —ALCHEMICAL SYMBOLS. (Glauber.)

Democritus (460-357 B.C.) is the earliest historical personage connected with alchemy, but it is not known how much of the alchemical knowledge of the ancients should be assigned to him. His name is found in the magic ritual of the Leyden papyrus (found in Thebes in the third century A.D.), and, according to Pliny, he received instruction in magic from Ostanos the Mede.

During the first centuries of the present era, the transmutation of copper into gold was thought to be an ascertained fact, and the works of Pliny, Dioscorides, Zosimus, Aeneas Gazaeos and Themistos Euphrades furnish records

of this belief, which probably originated in the production of alloys possessing the color of gold or silver. Kopp has pointed out that it is probable in early times a plating of gold or silver may have been considered an actual transmutation of the covered object.

In the early part of the Christian era, alchemy attained much notoriety and was fostered by the Church. In fact, the records of alchemy go on increasing from this era, and the savants of the time have left us fragments of their works. First among the alchemists of the early part of the Christian era is Zosimus, who lived in the third century. In his "Manipulations," comprising twenty-eight books, he speaks of the fixation of mercury, of a universal medicine, and of a tincture which possessed the property of converting silver into gold. Zosimus is spoken of with great esteem by the later alchemists, and his mystical language exercised a pronounced influence on the Alexandrians and medieval alchemists. Synesius, Bishop of Ptolemais, wrote commentaries on the works of Zosimus; he lived in the fourth century.

Olympiodorus, a native of Thebes, reproduced the philosophy of Thales and Anaximenes, and was the first to distinguish matter according to its combustibility. His works, however, do not contain any certain information with regard to definite operations.

Until the fourth century Alexandria had been the center of science and philosophy, but under Roman rule it gradually declined, so that at this time only the Temple of Serapis was left. This temple, which was the bulwark of medical and alchemical study, however, was destroyed in the reign of Theodosius, so that many books which would have been invaluable for the history of chemistry were lost through its destruction. The Serapeum of Memphis and the Temple of Ptah also were destroyed at the same time as the Temple of Serapis, and it is only due to the relations which before then were developed between the Egyptians and the Byzantine Empire that all acquaintance with

chemistry was not obliterated. Notwithstanding these catastrophes, the knowledge of some chemical operations continued to exist in Egypt, even tho the light of science was gone and adepts no longer taught their cult, and the conviction that the base metals could be transmuted into gold and silver, with its alluring possibilities, still remained a feature of Egyptian thought.

At the period when ignorance and barbarism prevailed through every part of the Roman Empire, Greek learning found an asylum among the Saracens. About the middle of the eighth century the second prince of the Abbassidean dynasty, the caliph Al-Mansur, founded the city of Bagdad and the light of philosophy dawned upon Arabia. Al-Mansur studied astronomy under the direction of two Christian physicians at his court, and offered liberal rewards to those who would undertake the translation of the Greek works on philosophy and science, which work was executed by the Christians then resident in Bagdad. He also founded a university at Bagdad, and pupils and professors flocked to it from all parts. Greece, Persia and India were taxed to help the Arab mind, India especially providing many alchemical notions.

The succeeding caliphs, Harun al Raschid and Al-Mamun, also were liberal patrons of learning of every kind, and under the caliphate of the latter the light of philosophy shone forth in meridian splendor. Science continued to enjoy the protection of the Saracen princes even after the empire was divided into several caliphates, and was, by means of their conquests, disseminated throughout the greater part of the world. From the beginning of the ninth to the end of the thirteenth century, when the power of the Saracens yielded to that of the Turks, schools of learning flourished in the empire, and the college at Bagdad contained 6,000 masters and scholars at the beginning of the twelfth century.

About the year 1000, twenty schools were instituted at Cairo and learning was imparted to a multitude of pupils.

Academies were also founded in Africa and Spain, and these were distinguished by eminent philosophers when barbarism universally prevailed among the western Christians. The library of the University of Cordova contained 280,000 volumes, and it is said that this university produced 150 authors.

Altho Islamism prohibited magic and all arts of divination, alchemy applied to the preparation of medicines was ardently studied and it found its way to the other Western nations, where from the Arabian universities in Spain it attained its full development in the thirteenth century.

The first of the "alchemical adepts" who appeared during the Christian era was the so-called founder of experimental chemistry, Abou Moussah Djafar al Sofi, afterward known to Western nations by the name of Geber. This alchemist is supposed to have lived in the eighth century, but his life is involved in hopeless obscurity and he has sometimes been confused with Dschabir of Tharsis. However, some historians of chemistry have ranked him first among the chemists and alchemists who flourished prior to the time of van Helmont, and it has been remarked that "Geber is to the history of chemistry what Hippocrates is to the history of medicine."

No less than 500 treatises have been attributed to Geber, and these are supposed to have included all the physical sciences; but the recent researches of Berthelot and others have proved that the Latin writings hitherto ascribed to Geber could not have been written by him. The oldest of these writings, the "*Summæ Perfectionis magisterii in sua natura Libri IV*," was not written till the middle of the fourteenth century, and it appears that the "*De Investigatione perfectionis Metallorum*," which was formerly thought to contain two important literary productions of Geber—his testament and a tract on the construction of furnaces—belongs to an even later date.

Berthelot further has shown that the Arabic manu-

scripts of the authentic Geber prove that he did not really profess the remarkable knowledge attributed to him, but that he adhered to the Greco-Alexandrian alchemists. His real views were mystical. For instance, he believed in the influence of the planets upon the metals, and his reasoning was mostly from premises which now appear defective. The Latin treatises, with which, until the investigations of Berthelot, the name of Geber has been connected, contain views on sulphur and arsenic, and on the transmutation of metals; in fact, they would make it seem that the object of his work had been the discovery of the Philosopher's Stone, but it is now known that these writings contain the collected knowledge of the four or five centuries after the time of Geber.

Rhazes, whose true name was Mohammed-Ebn-Secharjah Aboubekr Arrasi, was a celebrated disciple of Geber. He was born about the year 850, and no less than 226 treatises are said to have been written by him. These writings discuss the influence of the stars on the formation of metallic substances beneath the earth, and contain, some assert, the first mention of borax, orpiment, realgar, and certain combinations of sulphur, iron and copper, as well as some salts of mercury and compounds of arsenic (Figuier). He believed in the transmutation of metals and undertook to perform a transmutation before Emir Almansour, Prince of Khorassan, after the latter had spared no expense in providing the necessary apparatus and materials for the accomplishment of the "magnum opus." He failed miserably, however, and subsequently died in poverty and obscurity.

The next great Arabian scientist was the illustrious Ebn Sina, generally called Avicenna, who was born about 980. He is believed to have died in the year 1036, altho several Oriental peoples assert that he is still alive and enjoying the nectar of perpetual life and untold wealth, results of the surcharged power of the Philosopher's Stone. Six or seven treatises on alchemy have been ascribed to

Avicenna. One of these, the "Tractatulus Alchimie," treats of the nature of mercury, which Avicenna regarded as the universal vivific spirit, capable of penetrating, developing and fermenting. Avicenna undoubtedly derived his chemical knowledge from Geber. According to Waite, he describes several varieties of saltpeter and treats of the properties of common salt, sulphur, orpiment, vitriol and sal-ammoniac.

Among the other disciples of Geber may be mentioned the Arabian physicians Avenzoar, Averrhoes, Maslama and Abukases, and the philosopher Alfarabi. Avenzoar, who lived in the eleventh century, is said to have made some additions to the knowledge of medicinal preparations, while Averrhoes, a physician celebrated for his personal virtues, attempted to improve the theory of medicine by the aid of philosophy and attained some prominence as a chemist. A North Persian physician, Abu Mansur, wrote a work on the principles of pharmacology, by which may be ascertained the chemical knowledge of the time, but it appears that the Arabian alchemists of the eleventh, twelfth and thirteenth centuries mostly devoted themselves to attempts at transmuting the base metals into gold. These alchemists, in the main, were of little prominence and contributed nothing new.

At the beginning of the seventh century almost the whole Western world was overwhelmed with intellectual darkness, and in the eighth century philosophy and learning seemed ready to expire among the Greek Christians. However, the spirit of barbarism which possessed many of the reigning emperors was not characteristic of the reigns of Michael, Bardas and Constantine Porphyrogenetes, all of whom, excited by the example of the Saracen caliphs, recalled and encouraged learning. Constantine was himself, in the ninth century, the pupil of the Byzantine scholar Michael Psellus, who contributed to the propagation of alchemistic ideas.

From the eleventh to the fifteenth century philosophy and

learning were much neglected in the Greek empire, but at the time when Constantinople was taken (1451) there were several learned philosophers among the Greek Christians. These were obliged to leave their monasteries, how-



Fig. 6 —THE 'GREAT SECRET,' SULPHUR AND MERCURY UNITING TO FORM THE PHILOSOPHER'S STONE.

ever, and this circumstance occasioned the return of Grecian learning into Europe; for after the Greek empire was destroyed by the Turks, the friends of literature and science fled into Italy, taking with them many of the Egypto-Greek and Arabian alchemistic doctrines.



Notwithstanding the fact that the decadence of Saracen power in Europe was rapid after the expulsion of the Arabs from Spain, yet for some centuries the influence of Arabic thought was great. The works of the Arabians were translated and widely disseminated, and the modes of their thought and work imitated. Then, too, the returned crusaders aided in the spread of Eastern learning and many industries were founded by them. They were particularly interested in alchemy, however, and as the nobles were impoverished and desired to replenish their treasuries, attempts at transmuting the base metals into gold became more than a craze—it became the cardinal point toward which all chemical knowledge was directed.

Many Christian princes were imposed upon by pretending possessors of the Philosopher's Stone. It is especially interesting to note that the first appearance of an alchemist at a German court was about the year 1063, when a baptized Jew announced to Adalbert von Bremen that he had acquired in Greece the knowledge of transmuting copper into gold.

It was during the thirteenth century that learned men gave their attention to the study of alchemy, and consequently the art reached a high degree of development. These scholars considered that the transmutation of the metals was a settled fact and maintained the existence of the Philosopher's stone, and some of them—Albertus Magnus, Thomas Aquinas, Roger Bacon, Arnold Villanovanus and Raymundus Lullius—greatly influenced the development of chemistry by their pursuit of alchemy in a scientific spirit.

Albertus Magnus (1193-1230) was a scholastic theologian, but his genius and curiosity did not allow him to pass by the Hermetic science without giving it attention; in fact, he was the first German chemist of prominence and is ranked as a skilful practical chemist for the period in which he flourished. He became a Dominican friar in 1221, and from this time he was an instructor in philoso-

phy, grammar, alchemy and natural history at Cologne, Paris, Hildesheim and Regensburg.

Michael Maier, a later writer on alchemy, states that Albert acquired the secret of the Philosopher's Stone from the disciples of St. Dominic and that he communicated it in turn to Thomas Aquinas. Maier further declares that for thirty years Albert employed his knowledge as an alchemist and astrologer to construct, from metals selected under proper planetary influences, an automaton having the power of speech. This was the curious Android, which was said to reply to every question proposed to it and which Thomas Aquinas destroyed under the impression that it was a diabolical machine.

Albert is also said to have suddenly reproduced the flowers and softness of spring in the midst of winter for the entertainment of William II., King of the Romans, when the latter dined in the monastic house at Cologne. The views of Albert are in the main those of the Arabian school, altho he added many new chemical facts. He mentions alum, caustic alkali, red lead, arsenic, green vitriol, iron pyrites and liver of sulphur. He knew that arsenic renders copper white and he was familiar with the method of purifying the precious metals by lead. He found that sulphur attacks all the metals then known except gold and designated the cause of this combination by the term "affinitas."

In his "De Rebus Metallicis et Mineralibus," Albert states that he tested some gold and silver, said to have been manufactured by an alchemist, and which resisted seven fusions, but that the pretended metal was reduced to a scoria by an eighth fusion. He distinctly recognised the possibility of transmutation, however, when the operations were performed on the principles of nature; and considered that all metals are composed of an unctuous and subtle humidity, incorporated with a subtle and perfect matter—that is, the metals are all essentially identical, differing only in form. In one portion of his "De Al-

chymia," he asserts that gold is produced by the action of pure sulphur on pure mercury, by the permanent action of nature and after more or less time.

Thomas Aquinas (1225-1274), "the universal and the angelic doctor," was a Dominican friar and disciple of Albertus Magnus, and taught at Paris and Naples. Several works on alchemy have been ascribed to him. In one of these, the "Thesaurus Alchemiae," he states that "the aim of the alchemist is to change imperfect metal into that which is perfect," and, moreover, asserts that such a transmutation is possible. The other works of this character attributed to him are "Secreta Alchymiae Magnalia" and "De Esse et Essentia Mineralium." He wrote on the manufacture of artificial gems and some of the terms still in use by modern chemists occur in the supposititious writings of Aquinas, as, for example, the term "amalgam" for alloys containing mercury.

Roger Bacon (1214-1294), "the wonderful doctor," was born at Ilchester, in Somersetshire, England, and studied at Oxford and Paris. It is said that he studied history, learned the Oriental and Western languages, and gained a knowledge of jurisprudence and medicine, subjects to which little attention was given in his time; and, in order to prosecute his studies without interruption, he assumed the monastic life in the order of St. Francis. He employed his time not in the controversies of the day, but in researches into the properties of natural bodies, and by the aid of mathematical training and experiment he acquired a knowledge of mechanics, statics and optics. His success in physics and in the construction of automata kindled a spirit of envy among the monks of his fraternity, and this led to the circulation of a report that he held converse with evil spirits, causing him to be imprisoned for ten years. He also knew how to use convex lenses for telescopic and microscopic purposes, and drew attention to the error which occasioned the Gregorian reformation in the calendar.

Bacon was familiar with many processes in chemistry,

and doubtless would have produced great discoveries in this science had he not been drawn aside from the path of true investigation by the philosophical "ignis fatuus" which led the philosophers of this age to attempts at transmutation. He believed in the Philosopher's Stone and his views on the transmutation of metals may be illustrated by the following quotation from his "Speculum Secretorum":

"To wish to transform one kind into the other, as to make silver out of lead, or gold out of copper, is as absurd as to pretend to create anything out of nothing. The true alchemists never held such a pretence. What is the real problem? The problem is, first, by means of art, to remove from the rough, earthy mineral a bright metallic substance, like lead, tin or copper. But that is only the first step toward perfection; and the chemist's work must not stop there, for, besides that, he must look for some means of getting the other metals, which are always present in the bowels of the earth in an adulterated condition. For example, the most perfect is gold, which one always finds in the native state. Gold is perfect because in it Nature finished her work. It is necessary, then, to imitate Nature, but here a grave difficulty presents itself. Nature does not count the cycles which she takes for her work, to which the term of life of a man is but as an hour. It is, then, important to find some means which will permit one to do in a little time that which Nature does in a very much longer time. It is this means which the alchemists call, indifferently, the elixir, the Philosopher's Stone, etc."

Bacon also stated that

"With the help of Aristotle's 'Secret of Secrets,' experimental science has manufactured not only gold of twenty-four degrees, but of thirty, forty and onward according to pleasure."

The application of the study of alchemy to the extension of life was another subject of study with Roger

Bacon, and he states that the operation by which the base metals are purged from the corrupt elements which they



Fig. 7 —THE PHILOSOPHER'S STONE, SHOWING ITS TWIN NATURE, AND SYMBOLIZING ALL ITS POWERS OVER NATURE.

contain till they are exalted into gold and silver, is considered by every adept to be calculated to eliminate the

corrupt particles of the human body, so that the life of mortality may be extended for several centuries. The chemical investigations of Bacon have proved valuable, but the above mentioned alchemistic ideas seem incomprehensible to moderns when contrasted with his other views and knowledge. Gunpowder-like mixtures were within his knowledge, and, according to some, he names sulphur and saltpeter as two constituents, while the third constituent he denominates under the anagram "luru mone cap ubre." He probably derived this knowledge from some Arabic source. The Arabs were acquainted with gunpowder-like mixtures as early as 1280, and the knowledge of the propelling force of such mixtures came about between 1313 and 1325. Guttman states that "the so-called ancient records concerning the invention of gunpowder should be approached with great caution," since manuscripts of doubtful date and origin have been inadequately translated to serve various nations as proofs of their claim to this invention.

Bacon found that saltpeter could be purified by solution in water and crystallization; he subjected organic substances to dry distillation and observed that inflammable vapors were produced; and he called attention to the fact that air was necessary for the burning of a lamp. All these facts, together with many others, Roger Bacon learned by experiment, and he is to be regarded as the intellectual originator of experimental research. His important works are as follows: "Opus Majus," "De Secretis Operibus Artis et Naturæ," "Radix Mundi," "Speculum Secretorum," "Secretum Secretorum," "Breviarum de Dono Dei" and "Alchimia Major."

The alchemistic tendencies of the thirteenth century are distinctly reflected in the work of the two celebrated adepts, Arnaldus Villanovanus (Arnold de Villanova) and Raymundus Lullius, yet much uncertainty exists in regard to the life of the latter and to the works ascribed to him. Nevertheless both exercised no small influence on their

generation and they were held in high esteem on account of their methods and labors. Arnaldus Villanovanus (1245-1310), whose birthplace is uncertain, studied medicine at Paris for twenty years, after which he traveled through Italy, visiting the various universities. He subsequently went to Spain and practised as a physician in Barcelona, but learning that Peter d'Apono, a friend, had been seized by the Inquisition, he withdrew to Sicily, where he wrote his tracts on medicine under the patronage of Frederick II., King of Naples and Sicily.

Arnaldus was, however, charged with magical practises, and in 1317 the Inquisition of Tarragona condemned his books to be burned on account of the heretical sentiments they expressed. He was an adherent of the Arabian school, believing in the composite nature of the elements and in the transmutation of the metals, and his skill in Hermetic philosophy was recognised by his contemporaries, one of whom wrote, "In this time appeared Arnold de Villeneuve, a great theologian, a skilful physician and wise alchymist, who made gold, which he submitted to all proofs."

Arnaldus believed that quicksilver was the medicine of all the metals, that sulphur was the cause of their imperfections, and that the Philosopher's Stone existed in all bodies. He was acquainted with oil of rosemary and oil of turpentine, and conducted distillations in a glazed earthen vessel with a glass top. He was probably the first to point out the poisonous nature of decaying flesh. He made external application of various mercurial compounds and understood some of the properties of alcohol. His knowledge of poisons was extensive. The principal works of Arnaldus are "Rosarius philosophorum," "Flos florum," "Antidotarium," "De Vinis" and "De Venenis."

Raymundus Lullius (1235-1315) was descended from an old and noble Catalonian family, and led a varied career. According to Waite, in his "Lives of the Alchymistical Philosophers," he "united the saint and the man



of science, the philosopher and the preacher, the apostle and the itinerant lecturer, the dialectician and the martyr; in his youth he was a courtier and a man of pleasure; in mature age he was an ascetic who had discovered the universal science through a special revelation from God; after his death he was denounced as a heretic and then narrowly escaped beatification as a saint." He was probably initiated into the secrets of alchemy by Bacon and Arnaldus.

In all about 500 works have been ascribed to Raymundus, but there is very great uncertainty whether he is identical with the grammarian and dialectician of the same name, and, moreover, the errant life which he led could have afforded him few opportunities for the investigations involved in the search for the "magnum opus." Therefore it is supposed that many of his writings are spurious, altho three of his alchemical writings—the "Testamentum," "Codicillus seu Vademecum" and "Experimenta"—are regarded as genuine. His alchemistic doctrines are obscure and mystical, and this led many to think that wonderful facts were concealed in his treatises.

Raymundus attributed remarkable powers to the Philosopher's Stone, for he was able to say, "If the sea were of mercury, I would change it into gold." He also affirmed that health, long life and precious stones were to be procured through its means. The alchemist styling himself Raymundus Lullius was acquainted with nitric acid and used it to dissolve certain metals, and he prepared "aqua regia" by adding sal-ammoniac or common salt to nitric acid and was aware of its dissolving gold. Gruelin, in his "Geschichte der Chemie," states that Lullius was acquainted with spirit of wine and that he prepared vegetable tinctures by its use; and alum from Rocca, white and red mercurial precipitates, cupellated silver, marcasite and oil of rosemary are mentioned in the works on alchemy attributed to him.

Among the other alchemists of this period were Jean de Meung, the monk Ferarius and Pope John XXII. The





Fig. 8 — COINS AND MEDALS OF ALCHEMICAL 'GOLD.'

latter is claimed as an adept by the alchemists, but his orthodox biographers deny that he had any alchemistic inclinations. At his death in 1334, he left in his coffers eighteen million florins in gold and seven millions in jewels, and alchemists attribute these treasures to his skill in their science.

In the fourteenth and first half of the fifteenth centuries many alchemists were supposed to be in possession of the Philosopher's Stone. The prominent alchemists of this period were Nicholas Flamel, Peter Bono, Johannes de Rupescissa, Isaac of Holland and his son, Bernard Trevيسان, John Fontaine, Sir George Ripley, Thomas Dalton and Thomas Norton.

Owing to the fact that alchemy was encouraged at many of the European courts at this time, many charlatans sprang up, pretending to be able to make gold without limit, and in some cases the frauds attempted were discovered. Nevertheless alchemy was not suppressed and it found especial protection at the court of Henry VI. of England, notwithstanding the fact that in 1404, by an Act of Parliament, it was forbidden to make gold or silver, as the preceding monarchs had had to pay heavily for their encouragement of the art. As early as 1344, Edward III. had coins struck from gold said to have been made in the Tower and later large quantities of counterfeit gold coins were manufactured. The alchemist Le Cor seduced Charles VII. of France into a similar experiment during a war with England, which only resulted in increasing the national debt. This counterfeiting caused much discredit to be attached to alchemy and the result was that this was extended to chemistry itself. However, the knowledge of chemical compounds and operations was enriched during this period by some valuable experimental observations, and toward the beginning of the sixteenth century chemical knowledge was greatly extended.

## CHAPTER IV

### THE LATER ALCHEMISTS

UNTIL lately the marked progress in chemical knowledge which occurred toward the end of the fifteenth century and at the beginning of the sixteenth century was always associated with the name of Basilius Valentinus, but the authenticity of the writings ascribed to him has become more and more questioned, and they are evidently spurious in parts. He seems to have been born at Mayence about 1394 and to have been a monk of the Benedictine order; but, altho numerous works have been printed in his name, no further particulars concerning his life have descended to posterity. The important works which appeared under his name are as follows: "Currus Triumphalis Antimonii," "De Microcosmo deque Magno Mundi Mysterio et Medicina Hominis," "Tractatus Chymico-Philosophicus de Rebus Naturalibus et Præternaturalibus metallorum et mineralium," "Practica, una cum duodecim Clavibus et Appendice," "De magno Lapide Antiquorum Sapientum" and "Testamentum ultimum." It is impossible to extract from these works the knowledge gained and possessed by the original author, but, as von Meyer states, "there can hardly be any doubt that a large number of facts were recorded by the writer who lived about a hundred years before the books were published, this being especially the case in the 'Triumphal Car of Antimony,' in which we possess what for a time was a marvelous description of an element and its compounds."

In this work the extraction of antimony from the sulphide found in nature is described and the properties of antimony are in part mentioned. Antimony was used in purifying gold and its compounds were applied medicinally. It would appear that Basil Valentine was the first to prepare hydrochloric acid by heating together copperas and common salt; and that he was acquainted with the rectification of the distillate obtained from beer and wine by means of potassium carbonate, the use of precipitation as a method of experimenting, and the employment of the spirit lamp in certain operations.

Judging from some passages in the works ascribed to him, Basil Valentine made the first attempts at qualitative analysis, for he proved that iron was present in certain hard tins, gold in Hungarian silver, silver in Mansfield copper and copper in Hungarian iron. The language used in the works of Valentine is frequently obscured by mystical pictures and ideas, and, like others of his time, he often found it impossible to express his alchemistic thought in any language save that of far-fetched allegory.

The sixteenth century, a period of reformation, adventure and discovery, is characterized by the Paracelsists, who formed a transition from the alchemists of the Arabic school to the iatro-chemists. The latter had other objects of research than the alchemists, but as some of the Paracelsists and Medical Mystics were "hermetic philosophers," it is appropriate to refer to their alchemistic views here.

Paracelsus, the "Luther of Medicine," the "seer of Hohenheim," created a new school of alchemy. He considered that gold could be made by application of chemistry, but that the process is not to be compared with the method of producing gold by an exercise of the occult powers existing in the soul of man. On adopting this view, the Paracelsists with alchemistic tendencies abandoned experimental investigation and sought within themselves the great secret of alchemy.

Libavius, who criticized the mystical writings of the Paracelsists, nevertheless fully believed in the transmutation of the metals, and even van Helmont, the most distinguished of the iatro-chemists, went so far as to testify that he himself had effected the transmutation of mercury into gold. In his work, "De Vita Eterna," according to Waite, van Helmont makes the following declaration:

"I have seen and I have touched the Philosopher's Stone more than once; the color of it was like saffron in powder, but heavy and shining like pounded glass. I had once given me the fourth part of a grain. I call a grain that which takes six hundred to make an ounce. I made projection therewith, wrapped in paper, upon eight ounces of quicksilver, heated in a crucible, and immediately all the quicksilver, having made a little noise, stopped and congealed into a yellow mass. Having melted it in a strong fire, I found within eleven grains of eight ounces of the most pure gold, so that a grain of this powder would have transmuted into very good gold nineteen thousand one hundred and fifty-six grains of quicksilver."

He states further that he performed a similar operation in public many times, and consequently believed in the certainty of the art, altho he did not possess the secret of making the transmuting agent. Other chemists of the sixteenth century, as Agricola and Sennert, were not avowed alchemists, yet they did not oppose views respecting the transmutation of metals. The last important iatro-chemist, Tachenius, alone contended against the ennobling of metals. His instructor in Leyden, Franz de la Boe, accepted the belief of his times in regard to transmutation.

In the reign of James I. of England reports were circulated that an artist, Butler, had performed several transmutations in London by means of a red powder secured from an Arabian alchemist, and later he is said to have accomplished wonderful cures with a Hermetic medicine.

Van Helmont attests these miracles, some of which he had the opportunity of witnessing.

After chemistry had assumed its proper position as a science in the Phlogistic Period and its study was neither obscured by attempts at transmutation nor limited to the preparation of medicines, many experimenters still remained convinced of the possibility of converting individual metals into one another. Altho alchemical work was kept secret to a great extent and was looked down upon, yet expressions of belief were far from being uncommon, even among such chemists as Robert Boyle, Johann Kunckel, Homberg, George Stahl and Hermann Boerhaave. In his old age, however, Stahl advised and warned against the pursuit of alchemy, and Boerhaave, after considerable experimental work, showed the falsity of many of the views held by the alchemists.

For example, the alchemists asserted that quicksilver could be fixed in a fireproof, metallic condition without the addition of any other substance, but Boerhaave disproved this by keeping quicksilver at a somewhat raised temperature in an open vessel for fifteen years without noting any change, and when he heated the quicksilver at a higher temperature in a closed vessel for six months no change was observed. Ernst von Meyer states in his "History of Chemistry" that "after his (Boerhaave's) time no notable exponent of chemistry—which had now attained to the rank of a science—spoke" in support of the alchemistic views, "but all the greater was the number of cheats and swindlers who cultivated the lucrative field of gold-making even during the eighteenth century. The conviction of the impossibility of transmutation, which was at that time establishing itself among scientific chemists, made its way but slowly into outer circles. Credulity and the hope of obtaining riches for nothing were the means of leading many into very doubtful paths, even so late as the end of the eighteenth century and the beginning of the nineteenth. The final echoes of the alchemistic

problem which had for so long a period of time held the cultured of every nation in a state of tension and had even blinded eminent scientific men only appear to have died away during the last decades of the nineteenth century."

The statements of witnesses and conductors of alleged transmutations are often impressive and convincing, and such testimony is the strongest of the supposed evidence in favor of gold making. Probably the most interesting of such records is that contained in the "Golden Calf (the World's Idol)" of John Frederick Helvetius, an eminent Dutch physician, written in 1667. In this work, Helvetius narrates the fact that he received from the "Artist Elias" a piece of the Philosopher's Stone the latter had in his possession, and that this piece—no larger than "a grain of rape seed"—transmuted six drams of lead into the finest gold. This gold was then taken to a silversmith, who first mixed four parts of silver with one part of the gold, "then he filed it, put aqua fortis to it, dissolved the silver, and let the gold precipitate to the bottom; the solution being poured off and the calx of gold washed with water, then reduced and melted, it appeared excellent gold, and instead of a loss in weight, we found the gold was increased, and had transmuted a scruple of the silver into gold by its abounding tincture." In the seventeenth century it appeared impossible to doubt such testimony; and at that time it was not known that the articles made from alchemistic gold were but worthless alloys, prepared for fraudulent purposes.

Among the other hermetic philosophers and adepts of the seventeenth and eighteenth centuries, may be mentioned: Jean d'Espagnet, author of a treatise on mystical alchemy; Alexander Sethon, who suffered from exposure of his "power"; Michael Sendivogius, who made gold by projection in the presence of Emperor Rudolph II. at Prague, and at Varsovia and Wurtemberg; Busardier, who left a powder when he died, one grain of which was used by Emperor Ferdinand III. for converting three pounds of

mercury into gold; Eirenaeus Philalethes; Pierre Fabre; John Obereit; Lascaris, who is recorded as having changed mercury into gold and gold into silver; and Delisle. Alchemistic efforts were especially encouraged during this period at the courts of a large number of German princes, many of whom were amateur alchemists themselves and who expended large sums of money in fostering gold-making. The priests of trickery were, however, finally exposed as frauds and rogues, and a dire punishment was meted out to them, almost without exception.

It has been mentioned that the alchemistic ideas, with the transmutation of metals as their leading tenet, originated in Egypt, where they were first fostered by the initiates of the "Sacred Art"; and that the conversion of the sacred art of Egypt into alchemy resulted through contact with European thought and ecclesiastical mysticism. The Egyptian priests taught the unity of nature and asserted that a fundamental similarity existed between heavenly and terrestrial things; but alchemy, while its argument rested on a supposed familiarity with Nature's methods, and postulated an orderly and simple universe, applied moral conceptions to material phenomena and pursued a policy, rich in fantastic detail, dictated by fanciful conceptions.

The original and central aim of alchemy was the production of a substance which was variously designated as the "Philosopher's Stone," "the one thing," "the essence," "the great elixir," "the great magisterium," "the red tincture," "the stone of wisdom," "the heavenly balm," "the divine water," "the virgin water," "the phoenix," "the lion," "the old dragon," "the basilisk," and "the carbuncle of the sun." This substance was supposed to have the power of transmuting base metals into gold; but other powers were attributed to it also, and the alchemist undoubtedly regarded it as "the soul of all things." After the eighth century, the Philosopher's Stone was reputed



to possess the power of curing all diseases and was styled "the great panacea."

This belief in its powers came into existence gradually owing to the Western alchemists attaching too literal an interpretation to some of the Arabian descriptions of its powers; for instance, Geber termed the base metals invalids which he would cure (transmute) by means of the Philosopher's Stone. At a much later date (about 1600), it was claimed that the Philosopher's Stone could transform quartz into gems, change a thousand pearls into one pearl of great beauty, and render glass malleable. It was also said to possess the power of imparting moral culture and redemption from sin.

The descriptions of the "one thing" differ widely and the alchemists could describe it only in contraries. Some spoke of it as a red powder, others stated that it possessed a peach-blow color, and many affirmed that it was of a gray appearance. Paracelsus described it as a very stable, red substance, transparent as crystal, pliable as gum, and yet as fragile as glass. When pulverized, it was said to resemble saffron. Philalethes states, in his "Brief Guide to the Celestial Ruby":

"The Philosopher's Stone is a certain heavenly, spiritual, penetrative, and fixed substance, which brings all metals to the perfection of gold or silver, according to the quality of the medicine, and that by natural methods, which yet in their effects transcend Nature. . . . Know, then, that it is called a stone, not because it is like a stone, but only because, by virtue of its fixed nature, it resists the action of fire as successfully as any stone. In species it is gold, more pure than the purest; it is fixed and incombustible like a stone, but its appearance is that of a very fine powder, impalpable to the touch, sweet to the taste, fragrant to the smell, in potency a most penetrative spirit, apparently dry and yet unctuous, and easily capable of tinging a plate of metal."

The processes given for preparing the "Great Magisterium" are also numerous and varied. The methods whereby the agent is itself perfected, and the processes wherein the agent effects the perfecting of the base and imperfect things, were divided into ten or twelve "Gates," or stages, by the alchemists. The prime requisite was the securing of the crude material to be employed. This was called the "*materia prima cruda*," "*terra virginea*," etc., and altho it was thought to occur in very large amounts, its identity was unknown and the procuring of this substance was considered to be the really difficult part of the undertaking.

From the "*materia prima cruda*" was to be obtained the "*materia prima matura*," a substance also known as the "*mercurius philosophorum*," or "azoth," to which was then to be added "*auro philosophorum*." This mixture was then digested at a low heat for some time without the presence of the air, in the "*ovum philosophicum*," to procure the "raven's head," or "*caput corvi*," a black substance which, through long digestion, became transformed into the "swan," a white body. The latter was then exposed to a higher temperature to produce the Philosopher's Stone. The various "Gates" were known as calcination, dissolution, conjunction, putrefaction, congelation, citation, sublimation, fermentation and exaltation.

The Alexandrians believed that the metals were alloys of varying composition and, consequently, that the transformation of one metal into another was possible, either by means of the addition of other substances or the expulsion of some present; and the Western alchemists regarded all metals as compounds. For example, Arnaldus Villanovanus and Raymundus Lullius assumed mercury and sulphur as their constituents, and the latter asserted that every substance is composed of these two substances. Under the term "*mercurius*," or mercury, the alchemists saw the cause of metallic glance and malleability, while the term "sulphur" was used to express the idea of trans-

mutability and also combustibility; and the various metals were regarded as compounds of these substances in different proportions.

For instance, gold, the most perfect metal, which Nature was thought to form slowly in the earth, was considered to be a compound of much mercury with only a small amount of sulphur. Therefore, considering that all other metals differed from gold only in the proportions in which mercury and sulfur were present, the alchemists sought for an agent whereby these proportions could be changed and gold produced. Introspection preceding observation gave rise to the alchemistic views of the universe and natural phenomena, and, to quote M. M. Pattison Muir, "the change from alchemy to chemistry is an admirable example of the change from a theory formed by looking inward, and then projected on to external facts, to a theory formed by studying facts, and then thinking about them."

Altho many of the theories of the alchemists were ridiculous and much unimportant material was accumulated by them, yet they untiringly pursued their quest, their views were connected with their practice, and, as Muir observes, "there was a constant action and reaction between their general scheme of things and many branches of what we now call chemical manufactures." The result of this was that some progress, worthy of account, was made in the knowledge of applied chemistry during the alchemistic period.

Metallurgy was not the least of these. Three new metals—antimony, bismuth and zinc—were discovered in the second half of the Age of Alchemy and the knowledge of the properties of the metals already known was increased; but few alterations were made in the methods of extracting and purifying the metals. As might be expected, the greatest importance was attached to the treatment of gold and silver ores; and quite accurate balances

came to be used as a result of the attention given to the yield of the noble metals. For a long time, gold was obtained in a pure condition just as it was in earlier times—that is, by the use of lead; but later it was ascertained that it could be purified by fusion with stibnite (antimony trisulfide), and in the time of Albertus Magnus it was found that gold and silver could be separated by treatment with nitric acid. Prior to this time, the cementation process of the ancients was employed for effecting the separation of the noble metals. Silver was extracted by fusion with lead, a method in use in Pliny's time.

Mercury was obtained by roasting its ores in furnaces and by distilling sublimate (mercuric chloride) mixed with caustic lime; it was used in extracting the noble metals, in gilding, and in alchemical research. Zinc and bismuth are mentioned in alchemical literature, and it would appear that zinc was used in the early medieval times; however, these metals were not used technically. Cobalt ore is also sometimes mentioned.

In the fifteenth century, copper was prepared by immersing plates of iron in solutions of bluestone (copper sulphate), but there are no important improvements to record in the methods of extracting and preparing iron, lead and tin. However, the various degrees of hardness and softness of iron were known at an early period, and the deportment of copper, iron, lead and tin when subjected to heat and to the action of acids was studied throughout the alchemistic period.

Ceramics advanced to no little degree. In ancient times glass had been colored by adding various oxides of metals to the fused mass, but in this age it was learned that the colors could be burned in—a decidedly important discovery. It was also found that the use of glazes containing lead and tin for earthenware vessels was advantageous for certain purposes.

Dyeing became better understood. Several important dyes were introduced during the alchemistic period. Or-

chilla, which was known in ancient Rome, was brought from the East about the thirteenth century, and cochineal was introduced by the Arabians. Indigo also began to be used during this period. Alum was employed almost entirely as the mordant in dyeing.

Inorganic Compounds were more thoroughly studied. Nitric and sulphuric acids were obtained at an early date. The former was first prepared by the distillation of a mixture of saltpeter, bluestone and alum, but later it was found that it could be produced from saltpeter and sulphuric acid; and sulphuric acid was prepared by distilling a mixture of iron vitriol and pebbles, and by burning sulphur, after the addition of saltpeter, under a hood fitted with a side tube for the overflow of the acid produced. When sulphur is burned alone, a gas now known as sulphur dioxide is produced, and it is known that the water solution of this gas was often confounded with sulphuric acid. Geber prepared sulphuric acid by heating alum, but failed to study its properties other than finding that it was a powerful solvent. At a much later date, hydrochloric acid was prepared by heating common salt and green vitriol. This acid, which was known as "*spiritus salis*," was mixed with nitric acid to prepare "*aqua regia*," a strong solvent which the alchemists thought closely approximated to the "*alkahest*," or universal solvent.

The alchemists were acquainted with a large number of salts, of which it was thought that solubility in water was a general characteristic; hence, the term "*sal*" included a large number of substances and was widely distorted. The term "*alkali*" is first mentioned in the Latin writings ascribed to Geber, but, according to von Meyer, "one seldom meets in the alchemistic age with a strict distinction between potash and soda, or between their carbonates, while, on the other hand, preparations of carbonate of potash obtained in different ways were regarded as dissimilar products. The distinction drawn by Abu Mansur

between 'Natrun'—*i.e.*, the soda found in Nature as a mineral deposit—and 'Qualia,' the alkali from the ashes of land plants, is, however, very noteworthy. These names have perpetuated in the German words 'natron' and 'kali.' The solvent power of the lyes obtained from



Fig. 9 —ALCHEMIST PREPARING SULPHURIC ACID.

the carbonates of potash and soda by the addition of lime, was made use of by the alchemists.

Among the salts known to the alchemists were alum, which was prepared from alum shale and widely used; iron and copper vitriols; saltpeter, salmiac and carbonate of ammonia. Saltpeter (potassium nitrate) was probably

used in early times in the manufacture of fireworks; it was known in various periods of this age as "sal petrosum," "sal nitri" and "nitrum." Salmiac, "sal ammoniacum," chloride of ammonia, was originally prepared from dung, altho some of the naturally occurring product of volcanic origin was used. Carbonate of ammonia was prepared by the chemists of the thirteenth century and was known to them as "spiritus urinæ"; later it was obtained from salmiac and alkali carbonate.

Other inorganic compounds known to the alchemists were nitrate of silver, chloride of silver, mercuric oxide, mercuric chloride, basic mercuric sulphate, mercuric nitrate, zinc oxide, zinc sulphate, antimony trichloride, basic chloride of antimony, antimony trioxide, potassium antimoniate, arsenious acid, peroxide of iron, oxide of copper and the lead oxides. As before mentioned, the alchemists knew that gold dissolved in "aqua regia"; this solution, "aurum potable," was thought to possess wonderful medicinal effects. They also knew that silver could be precipitated from a silver nitrate solution by the use of mercury or copper.

The preparation of antimony from the sulphide by fusion with iron, is described in several of the works ascribed to Basil Valentine. It is mentioned in these works that antimony does not possess the properties of a metal in full degree, and that it is a variety of lead. In the fifteenth century, antimony was used in certain alloys, and the compounds of it then known were used in medicine. Arsenic was prepared in the thirteenth century by the Western alchemists, who considered that it was a "bastard metal." Arsenious acid was prepared as early as the tenth century, by roasting realgar, and was called "white arsenic." At a much later period, about the close of the Medieval Age, it was observed that arsenious acid occurs in the fumes from pyrites furnaces.

Mention has been made of some sulphur compounds, the sulphides of mercury (cinnabar) and antimony (stib-



nite) among others, which were found to be valuable materials for the production of sulphur and other bodies. These were grouped together as forming a particular variety of compounds, under the name of "marcasitæ" (Albertus Magnus), zinc blende, galena (lead sulphide), and iron and copper pyrites being included among them. The peculiarity which these substances had in common, that of giving off a product of such characteristic odor as sulphurous acid, when roasted, may have formed the main reason for assigning them to one group. It should be remembered, however, that the production of several metallic sulphides from their components had been observed (*e.g.*, the formation of cinnabar from quicksilver and sulphur), and this may be supposed to have contributed materially to a knowledge of their composition. Realgar and orpiment were known to the Arabian physicians.

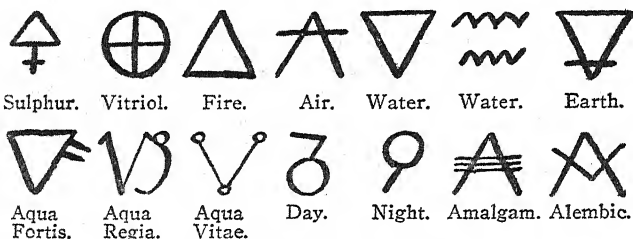
The alchemists were fond of using the names of animals as symbols of certain mineral substances, and of representing operations in the laboratory by what may be called animal allegories. The "yellow lion" was the alchemical symbol of yellow sulphides, the "red lion" was synonymous with cinnabar, and the "green lion" meant salts of iron and of copper. Black sulphides were called "eagles," and sometimes "crows." When black sulphide of mercury is strongly heated, a red sublimate is obtained, which has the same composition as the black compound; if the temperature is not kept very high, little of the red sulphide is produced; the alchemists directed to urge the fire, "else the black crows will go back to the nest."

Organic Compounds were also examined and their properties recorded. Notwithstanding the fact that the alchemists originally paid more attention to the properties of mineral bodies rather than to those of organic bodies, yet the study of the action of heat upon bodies when air is excluded and improvements in methods of distillation, led to the investigation, in a crude manner, of the products



of distillation and eventually to the discovery of definite organic compounds. Among the few organic preparations known to the alchemists, spirit of wine takes a prominent place. This compound was formerly designated by very different names; for instance, Marcus Graecus (eighth century) calls it "aqua ardens," the Latin translators of Geber's works refer to it as "aqua vitæ," and others mention it as "aqua vitis," "mercurius vegetabilis," "spiritus vivus" and "consolatio ultima corporis humani." The term "spiritus vini" first occurs in the writings ascribed to Basil Valentine, and the name "alcohol" was first used by Libavius at the end of the sixteenth century.

The symbols used to denote the metals have been referred to; among other signs employed instead of writing the names of substances, were the following:



SOME ALCHEMICAL SYMBOLS.

The Alexandrians employed two vessels in conducting a distillation, one for evaporating the liquid and the other for condensing the vapor, and this improvement resulted in the simplification of the method of manufacturing spirit of wine, and an extension of its importance in medicine and alchemy. The preparation of concentrated spirit of wine by repeated distillation and by rectification over dry carbonate of potash was described by Raymundus Lullius, who also examined the action of sulphuric acid upon spirit of wine. Spirits were generally dehydrated by rectifying at a low temperature, however, and in order to condense

the vapors completely they were passed through long condensing tubes, often of an extraordinary form.

At the close of the Middle Ages, the alchemists were acquainted with several ethers, which they prepared in an impure state by the action of acids on spirit of wine.

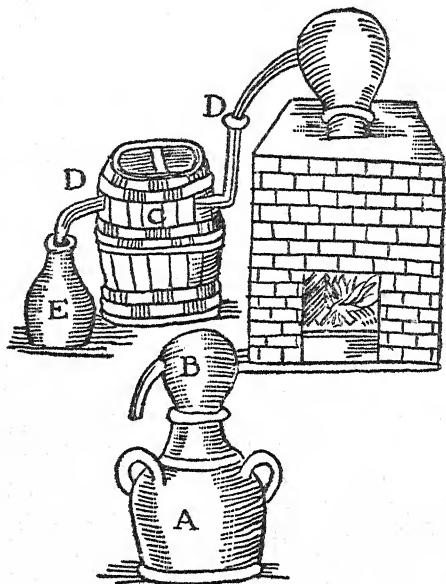


Fig. 10 —ALCHEMICAL STILL.

(a)—Copper still; (b)—Still head; (c)—Cooling medium; (d)—Condensing tube; (e)—Receiver.

One of the alchemical writers speaks of a spirit prepared in this way which has a "subtle, penetrating, pleasant taste, and an agreeable smell." This probably referred to ethyl oxide, or ethyl ether, a compound prepared by various chemists in the sixteenth and seventeenth centuries.

It has been mentioned that the only acid with which the ancients were acquainted was vinegar—that is, an



Fig. 11 —IMPROVED DISTILLING APPARATUS.

Frontispiece of Hieronymus Brunschwick's 'Liber de arte distillandi de compositis.'

impure wine vinegar. The alchemists, however, learned to concentrate vinegar, and it is to them that is owed the first production of acetic acid by distillation. The

alchemical views concerning the formation of acetic acid from alcohol are vague and it was frequently confounded with the acids observed in plant juices.

The belief in the transmutability of metals was dismissed from chemistry when Lavoisier established the important generalization of the new chemistry, namely, that matter may be changed, but neither destroyed nor created (1770). Nevertheless, many have applied themselves to attempts at converting the bountiful metals into the agreed standard of exchange, but these experimenters have been for the most part men of limited chemical knowledge and experience, and, to quote Charles Baskerville, "a careful analysis of the motives actuating and methods pursued presents merely an inferior picture of the perfected practises we are gradually learning of as obtaining in that circle termed 'high finance.'" The alchemical literature of the nineteenth century is quite extensive, but is, in general, cabalistic and teeming with credulity, misconception, and misinformation.

At the present time, there is a strong inclination among chemists toward a belief in the mutual convertibility of chemically similar elements. This view is based on the supposition that all the chemical elements are combinations of different quantities of one primal element and on the peculiar conduct of certain recently discovered elements; in fact, the belief in the transmutation of atoms is in close agreement with the present theories of atomic disintegration, but this is based upon new discoveries and on correctly interpreted chemical problems, and not upon false deduction and experiment. It is, therefore, not to be confused with the earlier views, for even if the hypothetical primal element should be isolated, one aim of alchemy would be fulfilled, but the fulfilment would not be that whereof the alchemystical philosophers taught and dreamed.

## CHAPTER V

### THE PERIOD OF MEDICAL MYSTICISM: THE IATRO-CHEMICAL PERIOD

THE sixteenth century, one of epoch-making discovery, witnessed the differentiation of Chemistry from Alchemy. Up to this time traditional belief had dominated every branch of science and scientific inquiry had been pursued almost solely in the cloister; but now the great universities of Oxford, Heidelberg, and others in France and Italy, were beginning to make their influence felt, and the sciences found a foothold in these institutions. Then, too, these seats of learning favored the free exchange of thought, and the introduction of the art of printing resulted in the quick and wide dissemination of ideas. Consequently, the capacity for reflection and criticism spread, and the boundaries of human knowledge were enlarged.

A further aid to the development of the natural sciences was supplied by certain modern eclectic philosophers who perceived the defects and errors of ancient lore and philosophy, and burst the enclosure of authority by attempting innovations in philosophy. The inductive method was found to be of especial value in combating and controverting medieval belief, and by its means the experimental sciences came into existence.

It was believed that Chemistry should serve the interests of Medicine, and, therefore, there was a strong tendency toward a concatenation of the two. Medicine was, to a certain extent, regarded as a division of Applied Chemis-

try, and then it began to be viewed as the true end of Chemistry. The chemist was to discover, prepare and investigate medicines—duties which resulted in the carrying out of many careful researches and in the discovery of new compounds, while the physician was to study their action on the human economy. This fusion resulted in the birth of Organic Chemistry; and the application of men belonging to a learned profession to the problems offered by chemical phenomena, enriched both Medicine and Chemistry. This increase in knowledge gradually led to definite ideas, and the Iatro-Chemical Period thus formed a period of extension for Chemistry.

In the first half of the sixteenth century, a Suabian physician, Philippus Aureolus Paracelsus Theophrastus Bombastus von Hohenheim, better known as Paracelsus, a name which has always carried with it a mysterious suggestion of power, liberated Chemistry from the yoke of Alchemy and joined it with Medicine. He accomplished this during a period of ecclesiastical and national reformation—when Luther and Calvin were combating against superstition, when Copernicus was remodeling astronomy—and the changes he wrought, through his originality of thought and teaching, and freedom and vigor of expression, well entitle him to the appellation some have seen fit to give him, the "Luther of Medicine."

Paracelsus was born at Einsiedeln, Switzerland, on November 10th, 1493. His father was a physician, and Paracelsus received his first instruction in medicine from him; and at the age of sixteen he entered the University of Basel, where he studied for a short time. So desirous was he of penetrating into the mysteries of Nature, however, that he neglected books and took prolonged journeys through most of the known countries of the world, where he had many romantic and hazardous experiences, but nevertheless sought to glean every scrap of knowledge obtainable from literary and learned men, mechanics, metallurgical workers, occults, and every one with whom he





came in contact. He returned to Switzerland about 1525, and was recommended by Oecolampadius to the chair of physic at Basel. He commenced his career at this institution by publicly burning the works of Avicenna and Galen, and at once began his fight against the old medical school. He was forced to leave Basel, however, in 1527, after a quarrel with the Municipal Council, and withdrew into Alsace, whither his fame in medicine followed him. About 1530, he returned to Switzerland, and from this time he seems to have roved restlessly in Germany and Austria, until at last, in the year 1541, he died in the hospital of St. Sebastian, in Salzburg in the Tyrol. The character and ability of Paracelsus have been rated high by some, and extolled and abused by others, even his disciples.

One writer says of him: "He lived like a pig, looked like a drover, found his greatest enjoyment in the company of the most dissolute and lowest rabble, and throughout his glorious life he was generally drunk." It is true that his life offered a strong contrast to his mentality, but he was a man of noble character and intentions, a Christian humanist and ambulatory theosophist, who hoped to inspire mankind with a love of conscientiousness and veracity and to restore the suffering to health.

Paracelsus was active as a teacher, physician and writer, and over a hundred books have been attributed to him. These works cover many subjects—chemistry, medicine, astrology, botany, etc.—but it has lately been shown that much of the subject matter was not really his. The chemical knowledge and medical views of Paracelsus are best seen in the following works: 'De Tinctura Physicorum,' 'Archidoxa,' 'Paragranum,' 'Paramirum,' 'De morbis ex Tartaro Oriundis' and 'Grosse Wundarznei.' Two other of his well known works are 'Das guldin Flüss' and 'Testamentum Theophrasti Paracelsi.' An excellent collection of various editions of the works of Paracelsus, together with many commentaries and translations, is now



preserved in the Homeopathic Medical College of Philadelphia.

Paracelsus taught that "the object of chemistry is not to make gold, but to prepare medicines," and he considered that the operations which occur in the human body are chemical ones and that the state of health is dependent upon the composition of the organs and the juices they secrete. Medicine, Paracelsus asserted, rests upon four pillars, chemistry, philosophy, astronomy, and virtue. Organic bodies were composed of mercury, sulphur and salt, which corresponded to the physical "phenomena of volatilization, combustibility and solidification," but which were related in a higher sense to spirit, soul and body; and the increase and decrease of these principles from their normal amount caused illnesses.

For example, he states that an increase of mercury produces paralysis, that an increase of salt gives rise to diarrhea, and that gout results from the elimination of the sulphur of the body. Paracelsus maintained that each disease must be antagonized by specific medicines ("arcana"), and that the preparation of these remedies was the aim of chemistry. In inaugurating this method of combating disease, he employed many chemical preparations, among which were sugar of lead (lead acetate), corrosive sublimate (mercuric chloride), copper vitriol (copper sulphate), lapis infernalis (silver nitrate), and many anti-mony compounds.

In addition, he was the first to use oil of vitriol sweetened by spirit of wine, iron saffron and iron tinctures; and introduced improved methods of preparing various essences and extracts by means of spirit of wine. These additions to the medical treasury instigated apothecaries and physicians to engage in the study of chemistry; for the preparation of new medicines required a certain familiarity with chemical facts, and before the advent of Paracelsus, the apothecary had been a mere herbalist and storekeeper. It may be said, therefore, that pharmacy began here, and

that pharmacy as a distinct profession and subject of study was largely founded by Paracelsus.

There seems no doubt that Paracelsus discovered many facts which became of importance in chemistry. He distinguished metals from substances which had been classed with metals; his criterion of a metal was ductility, and he was therefore led to separate the metals from the half-metals—a foundation for a classification of the metals which lasted for many generations. He obtained the inflammable gas we now call hydrogen by the reaction between iron filings and sulphuric acid, tho it could not be said to be a discovery in the sense of preparing and identifying the gas. The work he did upon the preparation and application of various inorganic and organic compounds, led to an extension of the knowledge of chemical preparations.

The Paracelsists, who arose as a result of the labors of Paracelsus, appear to have been largely mystics, but included also physicians who were adherents to his school, alchemists, and charlatans. These disciples engaged in a violent contest with the ones faithful to the doctrines of Galen, and during the sixteenth century the medical world was in a state of agitation as a result of the controversies and polemical writings which resulted. This contest was decided, if not altogether in favor of Paracelsus, at least in that of the iatro-chemists.

Many of the disciples of Paracelsus imitated the roughness, the wandering life, and the charlatanism of their master. These men, among whom was Thurneysser, reproduced the ideas of Paracelsus, but were without his mental gifts and wrought harm by the careless use of poisonous preparations. Such acts induced legal action, and in some places the prescription of poisonous preparations was prohibited. Such was the case in Paris, for example, where the parliament put a stop to the use of antimonial preparations in medicine.

There were such prominent physicians and chemists,

however, as Turquet de Mayerne, van Mynsicht, Croll and Andreas Libau, who belonged to the school of Paracelsus, but regarded his doctrines from a critical standpoint and attempted to extract only the good they contained. In these endeavors to separate true scientific facts and doctrines from a mysticism and seeming charlatanism mar-  
ring the works of Paracelsus, they enriched both medicine and chemistry. Turquet de Mayerne (1573-1655) possessed an excellent knowledge of chemistry for this age, and endeavored to introduce the rational application of chemical remedies. Oswald Croll was the first to recommend the use of volatile salt of amber (succinic acid) and of sulphate of potash in medicine; and Adrian van Mynsicht brought tartar emetic into vogue.

Andreas Libau (Libavius) was born at Halle, and there studied medicine and practiced as a physician. He also acted as head of the "Latin School" at Rothenburg from 1591 to 1607, and later became director of the gymnasium at Coburg, where he died in 1616. Libavius had a wide knowledge of chemistry and made many valuable chemical discoveries. From tin he obtained its tetrachloride, by distilling it with sublimate; and to him belongs the merit of simplifying the method of preparing sulphuric acid, and of showing that the acid obtained in many ways—from alum, sulphate of iron, or sulphur and nitric acid—was the same substance (oil of vitriol). He also discovered sulphate of ammonia, and investigated the acetates of lead. He vigorously combated the defects in the doctrines of Paracelsus, and did much to indicate the meaningless nature and obscurity of the mystical and sophistic writings of the Paracelsists.

Libavius wrote the first text-book on chemistry, which put, clearly and in order, all the most important facts and theories of the science at the date of publication (1595); this work, which was published under the title '*Alchemia e dispersis passim optimorum auctorum . . . collecta, adhibitisque ratione et experientia quanta*

potuit esse methodo accurata explicata et in integrum corpus redacta,' was frequently reprinted and was held in high esteem for a long time. His other writings appeared under the title, 'Opera Omnia Medico-chymica' shortly before his death.

Libavius possessed a thoro general education and a sound judgment, yet he believed in many of the tenets of alchemy. This was mainly due, however, to the predilection of the period in which he lived, and did not prevent Libavius from serving the interests of chemistry to good purpose. It is important to mention that he made efforts to establish large and well-fitted chemical laboratories.

Paracelsus and his followers had turned chemistry into new lines, and the finest talent was enlisted in the ranks of the iatro-chemists, or medico-chemists, to whose work Paracelsus had given such impetus. The most distinguished of these iatro-chemists was Johann Baptist van Helmont, a celebrated physician, born at Brussels in 1577. At an unusually early age van Helmont applied himself to the study of philosophy and theology, and, to quote from an autobiographical fragment which he left (Brande), "In 1594, being then seventeen years of age, I finished my courses of philosophy, but upon seeing none admitted to examinations at Louvain who were not in a gown and hood, as tho the garment made the man, I was struck with the mockery of taking degrees in arts.

"I therefore thought it more profitable, seriously and conscientiously, to examine myself; and then I perceived that I really knew nothing, or, at least, nothing that was worth knowing. I had, in fact, merely to talk and to wrangle, and therefore refused the title of Master of Arts, finding that nothing was sound, nothing true, and unwilling to be declared master of the seven arts, when my conscience told me I knew not one. The Jesuits, who then taught philosophy at Louvain, expounded to me the disquisitions and secrets of magic, but these were empty

and unprofitable conceits; and instead of grain, I reaped stubble. In moral philosophy, when I expected to grasp the quintessence of truth, the empty and swollen bubble snapped in my hands.

"I then turned my thoughts to medicine, and having seriously read Galen and Hippocrates, noted all that seemed certain and incontrovertible; but was dismayed upon revising my notes, when I found that the pains I had bestowed, and the years I had spent, were altogether fruitless; but I learned at least the emptiness of books and formal discourses and promises of the schools. I went abroad and there I found the same sluggishness in study, the same blind obedience to the doctrines of their forefathers, the same deep-rooted ignorance." He therefore concluded that medical knowledge was not to be obtained from the writings of men or from human industry.

About this time he learned, from a chemist, the practical operations of the chemical art, and devoted himself with great zeal and perseverance to this pursuit, in hopes of finding in a chemical laboratory that knowledge which he had in vain sought for from books. The medical skill, which he by this means acquired, he employed in the service of the poor, and, in addition, he enriched chemistry by a great number of valuable observations. He died in Brussels in 1644.

Van Helmont possessed ready talents, read much, and by the aid of experiment, improved both chemistry and medicine; but his vanity led him into empirical pretensions and he had an intense inclination toward the supernatural—the result of his mystical studies and application to theology, especially to the pious writings of Thomas-a-Kempis and John Tauler. Thus did he who possessed powers of observation and perception unapproached before his time by any other observer, give expression to fantastic views upon the elements and vigorously defend the transmutation of the base metals into gold. He thought that wisdom is to be obtained only by humility

and prayer, and believed that he had once seen his soul as a brightly shining crystal.

He was convinced that dirty linen packed in a vessel with flour would in time produce mice, and that a toad's bones applied to an offending part was a certain anodyne. He boasted that he possessed a fluid, the "alcahest," which was capable of penetrating into bodies, producing an entire separation and transmutation of their component parts. No one, not even his son, saw this wonderful fluid, and its possession was a secret van Helmont cautiously guarded.

Van Helmont looked upon water as the chief constituent of all matter, and brought forward many arguments in support of his theory from the animal and vegetable world. That water was present in organic bodies he concluded from the fact of invariably procuring it as a product of their combustion. He believed that he contributed a strong proof of this by the following experiment: He took an earthen vessel of large dimensions, and filled it with two hundred pounds of dry earth, in which he planted a willow weighing five pounds. This was then duly watered with rain and distilled water for five years, at the end of which time he pulled up the willow and found that it weighed one hundred and sixty-nine pounds and three ounces. Moreover, the earth had decreased two ounces in weight. He therefore concluded that one hundred and sixty-four pounds of root, leaves, etc., had been produced from water alone, and that it was the only nutriment of plants. Fish, he asserted, live on water, and nevertheless, they contain all the peculiar animal substances; the latter are therefore produced from water.

Basing his belief on such imaginary proofs as these, van Helmont was convinced of the transformation of water into earthy matter. With respect to his views concerning the four Aristotelian elements, he denied altogether that fire could be of a material nature, but it is uncertain whether he regarded air as an element or not.

His conception of the elements also differed from those of Basil Valentine and Paracelsus, for mercury, sulphur and salt were not to be detected in the human body.

Until the time of van Helmont little was known concerning gases. Pliny had spoken of "spiritus," which possessed properties differing from those of ordinary air; and of terrestrial emanations, some of which were combustible, others unendurable. But even Basil Valentine looked upon all such as common airs with differing impurities. Paracelsus had observed the evolution of gas when sulphuric acid is poured on iron, but this had appealed to him only as a mere expulsion of air. Van Helmont, however, changed the whole aspect of the question and proved himself an investigator of the first rank when he opened out a new field for chemistry by his researches on gases. In his writings the word "gas" occurs for the first time, a word he probably derived from the German "gäsch," the foam which appears during the process of fermentation; and by this generic name he classed all such emanations as could not be brought into the liquid state. For example, the gases now known as hydrogen, carbonic acid, and sulphurous acid were distinguished by van Helmont from vapors, in so far that the latter were condensed to liquids upon cooling, while the former were not.

The views of van Helmont on the composition of substances also were far in advance of any of his predecessors, and he recognised much more clearly than his contemporaries the unalterability of matter in many instances. Van Helmont further showed that the same substance continued to exist in many of its compounds, as, for example, silver in its salts; and demonstrated by quantitative experiment that if one body combines with another and is then precipitated, the weight so obtained is equal to that originally taken; *e.g.*, he found that silica, when fused to a glass with potash and again precipitated by the addition of an acid, lost nothing in weight. He had there-



fore clearly grasped the fundamental idea of the theory of the conservatism of matter in certain cases.

When he came to consider physiological and pathological phenomena, van Helmont accepted the doctrines of Paracelsus only in part. As before mentioned, he considered that the presence of mercury, sulphur and salt in the human body was unproven; and held that the acid of the gastric juice brought about digestion, but that this produced illnesses if present in excess, as it could not then be neutralized by the alkali present in the bile, as under normal conditions, when the mixture took place in the duodenum. He therefore declared that diseases resulting from such incomplete neutralization should be treated by the prescription of alkalis or acids according to their nature. These views show a distinct advance upon those of Paracelsus, as van Helmont endeavored to decide theoretical questions by the aid of experiments with juices and other secretions of the body, thereby laying the first foundation of chemical physiology.

The footsteps of this iatro-chemist were closely followed by his son, Francis Helmont, whose 'Paradoxical Dissertations' are a mass of medical and theological paradoxes, scarcely to be paralleled in the history of literature. He did a service, however, by publishing the collected works of his father in 1648. These works, which appeared under the title 'Ortus Medicinæ vel Opera et Opuscula Omnia,' were translated into German, English and French, and passed through three Latin editions.

In Germany and the Netherlands, various other physicians, well equipped with chemical and medical knowledge, were also active in combating many evils and endeavored to separate true scientific doctrines from mysticism; among these were Daniel Sennert and Angelo Sala. Sennert, who was born at Breslau in 1572, was educated at Wittenberg, where he became professor of medicine, and died in 1637. He wrote "*Hypomneuma Physica*," in which he contradicts many of the Aristotelian principles;



and altho he was unable to disentangle himself from many of the false conceptions of the Paracelsists, he did much to reconcile the adherents of the Hippocratic school to the new medicine, indicating the efficacy of chemical remedies when properly used and pointing out that the new medicine did not ignore the facts learned empirically under the old system, but attempted to interpret them correctly.

Sala was born at Vicenza in 1576 and died in 1637. He had a wide knowledge of chemistry for the period in which he lived, and formed correct ideas with regard to the composition and deportment of many chemical compounds; for example, he states that salmiac is composed of carbonate of ammonia and hydrochloric acid, and that nitric acid may be expelled from its salts by means of oil of vitriol. The works on chemistry by Sala are as follows: 'Saccharologia' (1637), 'Hydrelæologia' (1639), and 'Opera medico-chymica' (1647, 1693).

Other influential men of this time were François de la Boe Sylvius, Otto Tachenius and Thomas Willis. Sylvius was born at Hanau in 1614, but his life was mainly spent in Holland. In learning and culture he far surpassed most of his contemporaries, and he ably filled the chair of medicine in Leyden until his death in 1672. Sylvius directed all his efforts to showing that the physiological and pathological processes occurring in the human body were purely of a chemical nature, and his views were in the main those of van Helmont, with the spiritualistic element omitted. He did not hesitate to prescribe preparations of antimony and mercury, nitrate of silver, mercuric chloride, and zinc vitriol for internal use in medicine. His "Opera omnia" were published in Paris in 1671.

Otto Tachenius, a devoted pupil and follower of Sylvius, was born at Herford in Westphalia and practised as a physician at Venice in the middle of the seventeenth century. He was the last iatro-chemist of importance who adhered to the doctrines of Sylvius, and was an investi-

gator of note. He made some valuable contributions to the knowledge of the composition of chemical substances, originating the first pointed definition of the term 'salt,' as a compound of an acid and an alkali, and studying the proportions by weight in which substances react chemically. One of his important observations is that in which he noted the increase in weight which takes place when lead is transformed into its oxide. Among the writings of Tachenius, the following two English translations are best known: 'Clavis to the ancient Hippocratical Physick or Medicine made by manual experience in the very fountains of nature, whereby through fire and water, in a method unheard of before, the occult mysteries of nature and art are unlocked and clearly explained by a compendious way of operation' (1677); and 'Hyppocrates Chymicus' (1677).

In 1659 appeared the 'Diatribes de Fermentation' of the English chemist Willis, who held that fermentation was a decomposition brought about by communication of a vibratory motion to the particles of must, and the resulting separation of their loosely combined components. This theory was developed by Stahl forty years later.

The iatro-chemical doctrines contributed much to the general advancement of the science of chemistry, but two mistakes were made by the iatro-chemists: they endeavored to explain, on chemical principles, all the changes and processes occurring in the body—an attempt which was futile for the chemistry of that day; and, secondly, they set too narrow a limit for chemistry, which was not destined to remain in a subordinate position. Consequently, their medico-chemical ideas were upset after the middle of the seventeenth century, altho the tenet of the Phlogistic Period—the phlogistic hypothesis, which predominated during most of the eighteenth century—was indicated by many of the iatro-chemists.

No mention has been made thus far of those distin-



Fig. 13 —MELTING FURNACE FOR IRON.

An illustration from Georg Agricola's '*De re Metallica libri XII*' (1546).

guished technical chemists—Georgius Agricola, Bernard Palissy and Johann Glauber—who promoted applied chemistry during the iatro-chemical age. This was made necessary, since they worked independently of the main iatro-chemical current and, in general, only fostered chemistry in its applications to industries.

Contemporaneous with Paracelsus, but forming a strong contrast to him, was the true investigator, Georgius Agricola, who was born at Glauchau, near Meissen, in 1494, and died while mayor of Chemnitz in 1555. Agricola was a noted physician, but devoted himself more particularly to the study of mineralogy and metallurgy, writing little on medical subjects and not troubling himself about the storm over the revolution of Paracelsus. His works, which are indispensable to the history of metallurgy and mineralogy, are characterized by clearness and intelligibility; they are as follows: *'De re metallica libri XII, quibus officia, instrumenta, machinae, ac omnia denique ad metallicam spectantia non modo luculentissime describuntur, sed et per effigies suis locis insertas, adjunctis Latinis Germanicisque appellationibus, ob oculos ponuntur, ut clarius tradi non possint'* (1546); *'De ortu et causis subterraneorum—de natura eorum quae effluunt ex terra—de natura fossilium—de veteribus et novis metallis—Bermannus, sive de re metallica dialogus'* (1558), and *'De mensuris et ponderibus, . . . de precio metallorum et monetis'* (1580). It was through these writings that the important metallurgical operations first became generally known; Agricola was also among the first to indicate a method by means of which it was possible to estimate approximately the amount of metal in an ore, and to explain intelligibly the manufacture of various preparations of industrial importance.

Vanuccio Biringucci, author of a work on metallurgy entitled *'Pirotecnica'* (1540), in which various technical processes are described, like Agricola, held aloof from the discussion of the iatro-chemical questions current in

his time. He gave directions for preparing ultramarine, distinguishing it from copper azure.

Bernard Palissy busied himself in the domain of the ceramic art, and succeeded in affixing durable enamels on earthenware vessels, especially on those of faience pottery. His observations on enamels, on the burning-in of colors, and on the use of various clays for pottery, are embodied in his work, 'L'Art de Terre.' His works are clearly written, and show that he contributed to the founding of agricultural chemistry and mineralogy, and that he combated every speculation not based upon observation and experiment; among these are his "Discours admirables de la nature des eaux et fontaines, tants naturelles qu' artificielles; des metaux, des sels et salines, des pierres, des terres, du feu et des emaux; avec plusieurs autres excellents secrets des choses naturelles" (1580); and the "Moyen de devenir riche et la maniere veritable par laquelle tous les hommes de la France pourront apprendre a multiplier et augmenter leurs thresors et possessions" (1636). Along with Agricola, Palissy was the chief exponent of experimental chemistry in his time.

The next name of importance is that of Johann Rudolf Glauber, who was born in Franken, Bavaria, in 1604, and died at Amsterdam in 1668, and who still shares a somewhat hazy popular fame as the discoverer of "Glauber's salt" (sodium sulphate). This compound, which is mentioned in his 'De Natura Salium,' published in 1658, was obtained from the residue left in the preparation of hydrochloric acid, and, under the name "sal mirabile," was prized highly by physicians. The collected works of Glauber were translated into English and published in a folio volume, containing three parts embodying twenty-six treatises, by Christopher Packe, in London, in 1689. In these treatises are found clear descriptions of the preparation of many chemical compounds, and intelligible explanations in theoretical points of chemistry. Glauber

also showed intelligence in questions of national and domestic economy, and on numerous occasions he sought to prove that Germany should work up and improve its own products, and not leave this for other countries to do.

He was, however, inoculated with the prejudices of his age, and was addicted to the fantastic extravagances of alchemy. In writing he sometimes affected the style of the older alchemists, and the following passage from a discussion on "concentrating and amending metals by niter" will show how humorously absurd some of his ideas were: "First a man is to be made of iron, having two noses on his head, and on his crown a mouth which may be opened and again close shut. This if it be to be used for the concentration of metals is to be inserted into another man made of iron or stone, that the inward head only may come forth of the outward man, but the rest of his body or belly may remain hidden in the belly of the exterior man. And to each nose of the head glass receivers are to be applied, to receive the vapors ascending from the hot stomach. When you use this man you must render him bloody with fire to make him hungry and greedy of food. When he grows extremely hungry he is to be fed with a white swan. When that food shall be given to this iron man, an admirable water will ascend from his fiery stomach into his head, and thence by his two noses flow into the appointed receivers; a water, I say, which will be a true and efficacious aqua-vitæ; for the iron man consumeth the whole swan by digesting it, and changeth it into a most excellent and profitable food for the king and queen, by which they are corroborated, augmented, and grow. But before the swan yieldeth up her spirit she singeth her swan-like song, which being ended, her breath expireth with a strong wind, and leaveth her roasted body for meat for the king, but her anima or spirit she consecrateth to the gods that thence may be made a salamander, a wholesome medicament for men and women."



In his 'Proserpine: or, the Goddess of Riches,' Part III, Glauber details "the fundamental process, how to make good gold out of silver, with profit, and how to separate good gold and silver out of iron, tin, copper, and lead."

Notwithstanding his adherence to mysticism, Glauber enriched chemistry in an eminent degree by his discov-

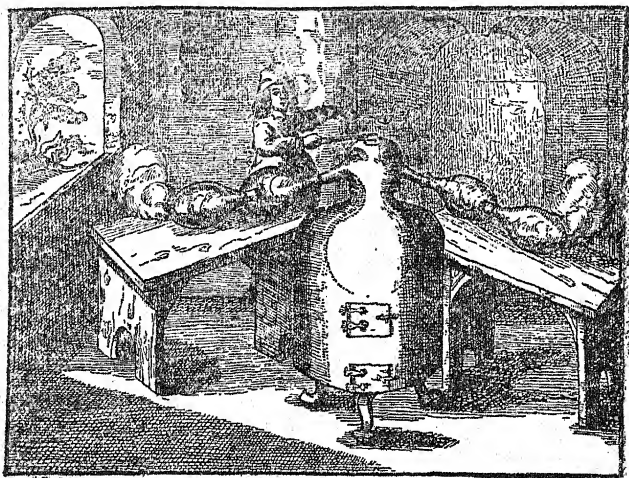


Fig. 14 —GLAUBER'S 'IRON MAN.'

eries. In attacking the question of the composition of bodies, he commenced by considering the conditions under which certain salts were produced, and the products of their mutual decomposition. Instead of preparing the chlorides of metals as heretofore, by heating the metal with sublimate (mercuric chloride), he treated the metal directly with hydrochloric acid, and concluded that the salt produced was merely a solution of the metal in the acid. This was a convincing blow to the time-honored

idea that the mercury of the sublimate had entered into the composition of the chlorides obtained.

Moreover, Glauber taught how to prepare hydrochloric acid from rock salt and oil of vitriol, and also fuming nitric acid from saltpeter and white arsenic. The preparation of hydrochloric acid, or 'spirit of salt,' is described in the first section of the second part of the '*Miraculum Mundi*.' Here also is given the method of obtaining 'sal mirabile,' the discovery of which first appeared in his '*De Natura Salium*.' To the discussion of the 'spirit of salt,' Glauber adds: "Plainly after the very same manner as we have taught spirit of salt to be prepared, so may also be made '*Aqua fortis*' (nitric acid). . . . Instead of salt take niter, and you will have '*Aqua fortis*.'" For a long time afterward the acid thus obtained (fuming nitric acid) was known as '*spiritus nitri fumans Glauberi*.'

The combination of acids with metals or alkalis was attributed by Glauber to a certain associative tendency, which he termed '*Gemeinschaft*.' He never employed the term 'affinity,' altho, as mentioned before, it was already the property of chemical literature. In Glauber's works we find a clear description of the preparation of sulphate of ammonia, formerly known as "*sal ammoniacum secretum Glauberi*," and the discovery of nitrate of ammonia, '*nitrum flammans*.' He was also the first to prepare chloride of arsenic, and ferric and plumbic chlorides, and to him is due a clearer knowledge of the chemistry of antimoniate of potash and other antimony compounds. He prepared impure zinc chloride by heating calamine strongly with hydrochloric acid; proved that copper sulphate, blue vitriol, is produced by boiling copper with oil of vitriol; and he was the first to mention a case of what is called double decomposition. His observations on the latter are of interest; to quote from one of his treatises, "*Aqua regia* which has taken gold into solution kills the salt of tartar (potash) of the liquor of flints



(silicate of potash) in such a way as to cause it to abandon the silica, and in exchange the salt of tartar paralyzes the action of the aqua regia in such a way as to make it let go the gold which it had dissolved. It is thus that the silica and gold are both deprived of their solvents. The precipitate is composed, then, at the same time of gold and of silica, the weights of which together represent that of the gold and of the silica originally taken."

With Glauber and Tachenius the period of Medical Mysticism closes. Both of them advanced chemistry by valuable observations, and in many of their chemical ideas and also in point of time, they really belong to the next, the Phlogistic, Period. The iatro-chemists had preserved a real science throughout a troublous and Philistine period, while their often fantastic speculations had caused no inconsiderable increase in the knowledge of chemical preparations. However, the advance in the knowledge of the composition of substances and in the observation of reactions first became pronounced toward the close of the Period.

In the works of Agricola, Biringucci, Caesalpino, Glauber and Palissy, stress is laid upon accurate description of technical operations, and it is from these works that knowledge accrues of the progress made in technical chemistry during the Iatro-chemical Period.

With regard to the extension of metallurgical knowledge, it is to be expected that the iatro-chemists were more interested in the salts prepared from metals than in the latter themselves, as there was always the possibility of chemical preparations proving of value in medicine. Nevertheless, especially in the works of Agricola, referred to before, it is found that a knowledge of the individual metals and of metallurgical operations became extended in the sixteenth century, as a result of the publication of what had hitherto been kept secret. The methods of obtaining iron became known through the works of Agri-

cola, and he was the first to describe the production of steel by the puddling process. It is interesting to note that steel was looked upon as a very pure iron. Of the other metals, the separation of gold and silver by means of nitric acid, and the amalgamation process became generally known; tin was employed in the sixteenth century for tinning iron; and altho zinc and bismuth were often confused with antimony, yet a better knowledge of them was acquired, and the tutty from zinc ores was employed for making brass.

One of the earliest treatises on glass manufacture is that by Antonio Neri, entitled *'L'arte vetraria distinta in libri sette; ne' quali si scoprono maravigliosi effetti e s'insegnano segreti bellissimi del vetro nel fuoco ed altre cose curiose,'* which was published in Florence in 1612, and in Latin at Amsterdam in 1681. In this work, Neri details his extensive experience, and it contributed to the diffusion of a knowledge of special ceramic operations. In the sixteenth century are found the first dependable observations on the manufacture of ruby glass by means of gold, and considerable skill was attained about 1600 in the production of artificial gems. Johannes Baptista Porta (1538-1615), of Naples, was the author of a treatise, *'De gemmarum adulteriis,'* in which recipes for preparing imitation precious stones were detailed. Agricola, in his treatise, *'De re Metallica,'* gives the first drawing of the interior construction of a glass furnace, and in this work as well as in Mathesius' *'Sarepta or Bergpostill'* (1654), are found explicit and interesting directions about the manufacture of glass as carried out in Venice, Germany and Bohemia.

In Bohemia, the glass industry began to flourish in the sixteenth century, the purity of the materials occurring there enabling glass manufacturers to produce the colorless glass for which the Bohemian glass-houses have long been famous. When the Venetian glass manufacture fell into decay, Bohemian glass replaced Venetian. The first

manufacture of glass in England is that of window glass, established in the fifteenth century, but the product was not satisfactory, and in the reign of Elizabeth, French artists were brought to London, and these carried on their trade of making window glass at Crutched Friars in 1557, while flint glass was first manufactured at a glass-house at Savoy House in the Strand. Mirror glass was manufactured at Lambeth by Venetian workmen brought over by the Duke of Buckingham in 1670. Glass works were established in France at an early date, but it was not until the eighteenth century, when workmen were brought from Germany, that a pure kind of French glass ware was produced. One of the important discoveries of this period was that of cobalt blue by Schürer, a Saxon glass blower, who obtained it on fusing the cobalteous residue from the manufacture of bismuth with glass; this latter became known as zaffre and smalt.

The efforts of Palissy in extending the knowledge of ceramics have been referred to, and it only remains to state that Johannes Porta was engaged in similar work in Italy about the same time. These savants devoted themselves with self-sacrificing assiduity to the production of glazed and colored faience, and laid the foundation of modern art pottery.

In dyeing a variety of vegetable colors were employed. Indigo and cochineal were imported from America and the East Indies, and numerous observations were made on dyeing processes. Drebbel learned that a solution of tin in aqua regia could be employed for fixing colors on cloth about 1630, and the methods of mordanting with alum and iron solutions were improved. The art of printing proved for dyeing, as well as for other arts, its great pioneer and propagator. In the middle of the sixteenth century, Plictho's "Art of Dyeing" was published. This treatise gave general instructions for dyeing all kinds of fabrics, and laid the foundation for that improvement of this art which soon after followed throughout Germany, France,

and England. It is interesting to note that the use of indigo was forbidden by the English Parliament in the reign of Queen Elizabeth, and that this act remained in full force till the time of Charles II.

Considerable interest was evinced in the distillation of liquors during this Period, and numerous works upon this subject appeared; among these were the following: Hieronymus Saler's '*Liber de arte distillandi de compositis*' (1500, 1512, 1527); John French's '*The Art of Distillation*' (1651); and Elsholtz's '*Distillatoria curiosa seu ratio ducendi liquores coloratos per alembicum*' (1674). Many improvements were made both in distilling apparatus and in the methods of distillation, and the distillation of brandy became an industry.

The word distillation up to the end of the fourteenth century meant the separation of the more light or subtle parts of anything from the more heavy or gross by a process of dropping. Thus Geber and others included the filtration of a liquid as a variety of distillation. The Latin word "*distillo*" applies to a dropping liquid, but such employment of the term does not appear after the fourteenth century in chemical works, altho the older use of "*distil*" is still found in ordinary writings, especially in poetry, and occurs in Fielding and Shakespeare. The process of distillation was classified in various ways; for instance, according to the source and mode of application of the heat, the shape of the alembic or distillatory vessel, and the direction impressed on the vapor upward or downward ('*distillatio ascensum vel decensum*').

The heat was applied in the form of the direct heat of a fire, or the heat conveyed through water or through sand, or the direct heat of the sun. Porta, about 1585, employed concave mirrors to concentrate the sun's rays (Fairley). Repeated distillation was often prescribed, as the purity of the distillate was thought to be increased by each distillation up to the fifth distillate, which was termed the "*quintessence*." An alcoholic distillate obtained in

this way from selected wine was considered to possess great medicinal value.

During the sixteenth and seventeenth centuries the distillation of fermented alcoholic liquids became subject to State supervision in many European countries. In Ire-



Fig. 15 —SALTPETER MANUFACTURE.

Plant for preparing saltpeter on a large scale (about 1600).

land, where it has been shown that the distillation of a spirit from fermented barley was practiced in 1170, up to 1556 the distillation of spirits was carried on without license or taxation. In the reign of Henry VIII, distil-

eries were established in Pembroke by Irish settlers, and it is considered likely that the soldiers of Henry II, 300 years previous, brought back with them the knowledge of whisky, or 'uisque-beatha.' The manufacture of 'aqua

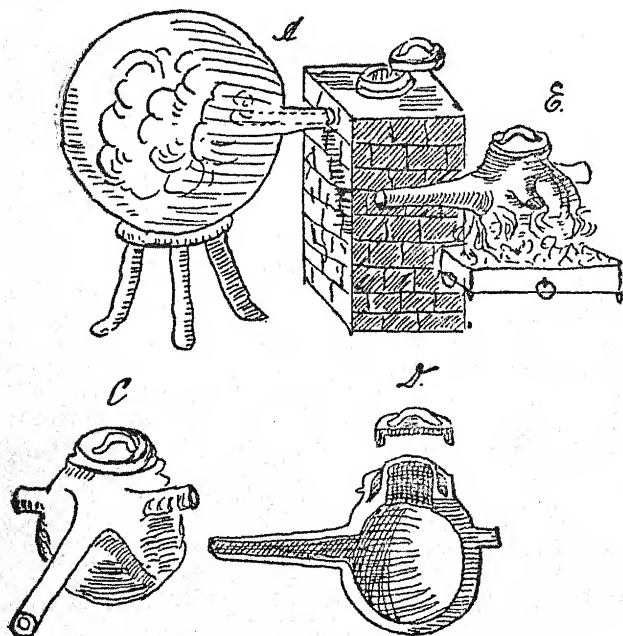


Fig. 16 —GLAUBER'S DISTILLING APPARATUS.  
(a)—Oven with distilling vessel installed; (c)—Form of distilling vessel; (d)—Cross-section of same; (e)—Method of heating by coal.

vitæ' from malt appears to have been common in Scotland and England in 1494, and, in the middle of the seventeenth century, the manufacture of spirits was made a source of revenue by excise duties on the amount manu-



factured. In the Tudor and Stuart period, licenses had been required to use stills.

The knowledge of chemical compounds, especially the preparation of inorganic compounds, showed decided improvements; and the beginnings of qualitative analysis are to be sought for in this Period, in so far that conclusions concerning the presence of one or another constituent were deduced from the appearance and behavior of precipitates and of salts which crystallized out from solutions. Glauber designed several forms of furnaces and casting vessels which were found to be useful in the preparation and investigation of a number of inorganic substances.

As a result of the attention paid to the products of vegetable and animal assimilation, organic compounds became known in rapidly increasing numbers, but the composition of these bodies remained quite undiscernible. It is worthy of note that many of the iatro-chemists assumed that "oil or fat contains a hidden acid," basing their conclusion on the old observation that fats were acted upon and changed by alkalies.

The importation of sugar from Spain, Portugal, Madeira, the West Indian islands, and Brazil soon made this article better known throughout Europe. Libavius in his 'Alchymia' (1595) mentions "Sacchari crystallini quod candi appellant," and he recommends a plan of purifying Madeira sugar by means of albumen, and Angelus Sala in his 'Saccharalogia' advises the use of egg albumen and lime water for this purpose.

Milk sugar, occurring in the milk of mammalia, especially in that of the herbivora, was first examined by Fabrizio Bartoletti in 1619; it was termed by him "manna s. nitrum seri lactis." It was more closely examined by Testi in 1698. Glauber noticed in 1660 that a granular sugar is contained in honey, raisins and in the juice of sweet cherries, but he did not point out that it differs from cane sugar.

## CHAPTER VI

### THE EARLY PHLOGISTIC PERIOD

HERETOFORE the inducements to a study of chemical phenomena had been successively a belief in the possibility of transmutation, and a conviction in the potency of heroic medicines prepared in the chemical laboratory. But from the middle of the seventeenth century onward another aim is manifest in the works of the masters; for, from the time of Boyle forward, the great end of chemistry was recognised as being the discovery of new chemical facts, with the object of arriving at the truth alone, and, thanks to the spirit of true investigation which had begun to extend itself to chemistry and the effect of the inductive method of Francis Bacon, chemistry assumed its proper place as a science.

As an approach is made to modern times, it becomes more difficult to define historically the successive phases of chemistry. The learned societies which were founded in the second half of the seventeenth and beginning of the eighteenth centuries, and whose periodicals furnished ever-accumulating data for the discussion of old and the initiation of new theories, and disseminated the results of chemical investigations in general, assisted materially toward the healthy progress of chemical science; but nevertheless firm obsequiousness to any one school of scientific thought was not to be expected, nor was it found.

The London Royal Society was founded by Charles II., and was incorporated by him in 1662, under a royal



charter, for the improvement of natural knowledge. The first volume of the 'Philosophical Transactions' of that society bears the date 1665, and ever since its foundation the Royal Society has been a nucleus around which has clustered the scientific genius of Great Britain. In 1666, the Academie Royale was instituted in Paris under the protection of Louis XIV., and its 'Memoires' began to appear in 1699. Other scientific societies—the Accademia del Cimento of Florence (1657), the Academia Naturæ Curiosum of Vienna (1652), and the Berlin Academy (1700)—also brought together those who were in sympathy through their devotion to knowledge, and by the interchange of their ideas thought was quickened and the advance of science aided. The reciprocal action of chemistry and allied branches of science upon each other was also promoted by bringing together their respective exponents, and the discussion of scientific researches helped more thoroly to sift the evidence on which their conclusions were based, and tended to promote increased accuracy and simplicity of thought and expression.

Altho the literature of the day bears record of many observations, isolated discoveries, and discussions on chemical problems, yet there was one problem which engrossed the attention of almost all philosophers during the seventeenth and eighteenth centuries, and this was the explanation of fire and the phenomena caused by fire. Notwithstanding the fact that here scarcely any two chemists were agreed in their conclusions, their modes of arriving at them showed remarkable similarity. Little note was taken of the proportions by weight in which substances entered into reaction, the qualitative side of phenomena alone being considered.

This period of about one hundred and twenty years, from Boyle to Lavoisier, may therefore be described as that of Qualitative Chemistry—a step toward the quantitative work of the Modern Period, and an immense step forward from the speculative and fortuitous chemis-

try of the preceding periods. It was a period of generalization, for just as fire was to be explained by the assumption of one general principle, 'phlogiston'—a doctrine which influenced chemists to such an extent that this period is characterized as the Phlogistic Period—so the general properties of acidity and causticity were to be viewed as conferred by one fundamental acid and one fundamental alkali respectively; and altho it was itself handicapped by erroneous views, the Phlogistic Period contributed largely to the refutation of alchemical and iatrochemical errors, and was a highly productive period for chemistry.

Robert Boyle (1627-1691) was the seventh son and fourteenth child of Richard, Earl of Cork. He was born at Lismore, in Munster. At eight years of age he was sent to Eton, where, says he, a perusal of 'Quintus Curtius' "conjured up in me that unsatisfied appetite for knowledge that is yet as greedy as when it was first raised." After about four years at Eton, Boyle went to his father's seat in Dorset and afterward traveled. He became a student at Geneva and continued his studies at the manor of Stalbridge from 1644 to 1654, when he settled at Oxford. In 1668 Boyle moved to London and was a prominent member of the then newly constituted Royal Society. He was elected president in 1680, but refused to serve, owing to a scruple he entertained as to taking oaths. In 1689 his health began to fail and he issued an advertisement restricting the visits of his acquaintances. He also had a board put up outside his house announcing when he received visits. Boyle's health had never been good; from the age of twenty-one he suffered from stone, and much feared that if it forced him to take to his bed the pain of it would become intolerable. He died, however, without pain, and almost without serious illness.

Boyle developed talent early, and at twenty-one he had already written on ethics and published several moral and religious essays. In 1665 he published his 'Occasional

Reflection upon Several Subjects,' which procured him the satire of Swift in 'A Pious Meditation upon a Broomstick, in the style of the Honourable Mr. Boyle.'

It would be needless to attempt to go over the whole ground of Boyle's work, altho there is much in it of interest even at the present time, as, for example, his papers on the 'Saltness of the Sea,' and the 'Nature of the Sea's Bottom,' and his 'Essay of the Intestine Motions of the Particles of Quiescent Solids wherein the absolute Rest of Bodies is called in question.' He was perhaps the first to draw attention to the desirability of studying the forms of crystals, and his paper on the 'Figures of Salts' contains many curious observations; in his 'Experiments about the Superficial Figures of Fluids, especially of Liquors contiguous to other Liquors,' he breaks ground which has taxed the energies of our greatest mathematicians. His 'Treatise on Cold' abounds with striking and original experiments; for example, he demonstrates the expansive power of freezing water by bursting a gun barrel filled with water and securely plugged, by placing it in a mixture of snow and salt, a freezing mixture which he himself introduced in England. His 'Essays on the Usefulness of Experimental Natural Philosophy' were of the greatest service in his time in furthering the cause of science by showing how the material interests of civilization may be promoted by its study; and, lastly, his tract on 'Unsucceeding Experiments' must have been, to quote Thorpe, "as the wine of gladness and the oil of consolation to many a despondent virtuoso."

Boyle was born in the year in which Bacon died; and Boyle's place in the history of science is that of the first true exponent of the Baconian method, and the 'Sceptical Chymist' is his greatest work. This work probably contains a greater number of well-authenticated facts than is to be found in any other chemical treatise of its day.

But the real merit of this work consists in its determined attack on the authority of the Peripatetics and

the Paracelsians. To quote from his own statement in 'The Sceptical Chymist':

"To acquaint you with divers of the conjectures (for I must yet call them no more) I have had concerning the principles of things purely corporeal: for though, because I seem not satisfied with the vulgar doctrines, either of the Peripatetick or Paracelsian schools, many of those, that know me, . . . have thought me wedded to the Epicurean Hypothesis (as others have mistaken me for a Helmontian). . . . I should tell you, that I have sometimes thought it not unfit, that to the principles, which may be assigned to things, as the world is now constituted, we should, if we consider the great mass of matter, as it was whilst the universe was in making, add another, which may conveniently enough be called an Architectonick principle or power; by which I mean those various determinations, and that skilful guidance of the motions of the small parts of the universal matter by the most wise Author of things, which were necessary at the beginning to turn that confused chaos into this orderly and beautiful world. . . . For I confess I cannot well conceive, how from matter, barely put into motion, and then left to itself, there could emerge such curious fabricks, as the bodies of men and perfect animals, and such yet more admirably contrived parcels of matter, as the seeds of living creatures."

Boyle is severe upon the affected mysticism of the Spagyrist. They may be as obscure as they like about their elixir, and the rest of their grand arcana, "yet when they pretend to teach the general principles of natural philosophers, this equivocal way of writing is not to be endured. For in such speculative inquiries where the naked knowledge of the truth is the thing principally aimed at, what does he teach me worth thanks, that does not, if he can, make his notion intelligible to me, but by mystical terms and ambiguous phrases darkens what he should clear up, and makes me add the trouble of guessing at the

sense of what he equivocally expresses, to that of learning the truth of what he seems to deliver."

Indeed, Boyle does not hesitate to say that the reason why the Spagyrist wrote so obscurely of their three great principles was, according to Thorpe, "that not having clear and distinct notions of them themselves, they could not write otherwise than confusedly of what they had confusedly apprehended: they could scarcely keep themselves from being confuted but by keeping themselves from being clearly understood—home thrusts which must have made many a Helmontian wince. The effect of such hard hitting is made evident on the most superficial comparison of the general style of chemical treatises immediately preceding Boyle's time with those published toward the close of the seventeenth century."

The 'Sceptical Chymist' compelled the decline of the doctrine of the 'tria prima,' and before the close of the century the Paracelsians were as much out of date as a Phlogistian would be to-day. Boyle indeed appeared to incline to the belief that all matter is compounded of one primordial substance—in other words, that all matters are merely modifications of the 'materia prima.'

To quote again from his 'Sceptical Chymist':

"I consider, that if it be as true, as it is probable, that compounded bodies differ from one another but in the various textures resulting from the bigness, shape, motion, and contrivance of their small parts, it will not be irrational to conceive, that one and the same parcel of the universal matter may, by various alterations and textures, be brought to deserve the name, sometimes of a sulphureous, and sometimes of a terrene, or aqueous body."

How closely he was in accord with the modern spirit is shown in this remarkable passage: "I am apt to think that men will never be able to explain the phenomena of nature, while they endeavor to deduce them only from the presence and proportions of such or such material ingredients, and consider such ingredients or elements as

bodies in a state of rest; whereas indeed the greatest part of the affections of matter, and consequently of the phenomena of nature, seem to depend upon the motion and contrivance of the small parts of bodies."

It was possible for Boyle to expose the shortcomings and fallacies of the then prevalent idea of Element or Principle: "I mean by elements, as those chymists, that speak plainest, do by their principles, certain primitive and simple, or perfectly unmingled bodies; which not being made of any other bodies, or of one another, are the ingredients of which all those called perfectly mixt bodies are immediately compounded, and into which they are ultimately resolved. I need not be so absurd, as to deny, that there are such bodies as earth and water, and quicksilver and sulphur: but I look upon earth and water, as component parts of the universe, or rather of the terrestrial globe, not of all mixt bodies."

This conception of an element gave the term a positive meaning.

Boyle also looked forward to the discovery of a much greater number of elements than was at that time assumed, at the same time maintaining that many of the substances then held to be elementary were not really so. Boyle was the first to state clearly that a chemical compound results from the combination of two constituents, and that it has properties entirely different from those of either of its constituents alone. He was, therefore, enabled to draw a sharp distinction between mixtures and chemical compounds, and to grasp clearly the main problem of chemistry—the investigation of the composition of substances. In doing this he had the solid ground of experience and experiment under his feet, and could always bring forward evidence for the probability of his views. His endeavors to get at the root of the composition of bodies gave an impetus to analytical chemistry, which before his time could hardly be said to exist; and we are at the same time indebted to him for fixing the



meaning of a "chemical reaction." Boyle appears to have been the first to employ the term analysis, in the sense in which it has since been used by chemists.

Also he devoted much attention to the inquiry of the cause of combustion and other similar phenomena, and altho his attempts at explaining these were not very successful, his experiments on the rôle played by air in combustion aided the later solution of the problem. His investigations on air and gases led him in 1660 to the well-known discovery of the law that "the volume of a gas varies with the pressure" (Marriotte educed this independently in 1677).

Boyle's writings, which were extensively read in his own time, are characterized by simplicity of style and clearness of expression; they offer, as von Meyer observes, "an agreeable contrast to the works of many of the other chemists of his time, who sought to hide their deficiencies in clear thought and accurate knowledge by metaphorical and mysterious language." In addition to other papers published in the 'Philosophical Transactions,' the following works of his, which were brought out both in English and Latin, are to be particularly mentioned: 'The Sceptical Chymist' ('Chemista Scepticus'), first published anonymously in 1661, and afterward in many editions with Boyle's name as author; 'Tentamina quædam Physiologica' (1661); and 'Experimenta et Considerationes de Coloribus' (1663). Editions of his complete works were published in London in 1700, 1725, and 1744.

A contemporary of Boyle who made important observations on combustion was Robert Hooke (1635-1702).

Hooke was born in the Isle of Wight and was originally intended for the Church, but he was of a weakly constitution, and much subject to headache, and owing to these causes the idea was finally abandoned. His leanings were first shown in a considerable aptitude, as a boy, for constructing mechanical toys. After his father's death Dr. Busby took him into his house and supported him while

at Westminster School. After leaving school he went to Christ Church, Oxford, and, in 1655, he was introduced to the Philosophical Society. Here his talents were speedily discovered and he was employed to assist first Dr. Willis and then Mr. Boyle. In 1662 he was made curator of experiments to the Royal Society, and when this body was established by charter he was one of the first nominated to fellowship. He obtained several professional posts and in 1665 he published in folio his 'Micrographia, or some physiological descriptions of minute bodies made by magnifying glasses, with observations and inquiries thereupon.' It was dedicated to Charles II.

It is usual to state that Hooke anticipated the modern view of the nature of combustion in this treatise; but it will appear from the following extract that whatever value may be assigned to his work, it cannot be claimed that he did more than recognize the part played by the air in the process, while still adhering to the conception of a 'sulphureous principle' which is lost by the body during combustion. Thus he observes:

"From the experiment of charring of coals . . . we may learn . . . that the air in which we live, move, and breath, and which encompasses very many, and cherishes most bodies it encompasses, that this air is the menstruum, or universal dissolvent of all sulphureous bodies . . . that the dissolution of sulphureous bodies is made by a substance inherent, and mixt with the air, that is like, if not the very same, with that which is fixt in saltpeter, which by multitudes of experiments that may be made with saltpeter, will, I think, most evidently be demonstrated. . . . The dissolving parts of the air are but few, that is, it seems of the nature of those saline menstrooms, or spirits, that have very much flegme mixt with the spirits, and therefore a small parcel of it is quickly glutted; and will dissolve no more; . . . whereas saltpeter is a menstruum, when melted and red-hot, that abounds more with those dissolvent particles, and therefore as a small



quantity of it will dissolve a great sulphureous body, so will the dissolution be very quick and violent. . . . It is observable, that, as in other solutions, if a copious and quick supply of fresh menstruum, though but weak, be poured on, or applied to the dissoluble body, it quickly consumes it: so this menstruum of air, if by bellows, or any other such contrivance, it be copiously apply'd to the shining body, is found to dissolve it as soon, and as violently as the more strong menstruum of melted nitre."

The completion of Hooke's theory was effected by John Mayow, who was born in the parish of St. Dunstan, London, in 1645. In 1674 he produced the treatise on which his fame rests; it is entitled '*Tractatus quinque medico-physici quorum primus agit de salnitro et spiritu nitro-aëreo, secundus, de respiratione, tertius de respiratione foetus in utero et ovo, quartus de motu musculari et spiritibus animalibus, ultimus de rhachitide*'; studio Joh. Mayow, LL.D. & Medici, nec non Coll. Omn. Anim. in Univ. Oxon. Socii. Oxonii e Theatro Sheldoniano, An. Dom. MDCLXXIV.'

Mayow's assumption—that atmospheric air contained a substance, the '*spiritus nitro-aëreus*' (also present in saltpeter), which combined with metals when they were calcined, and which sustained respiration and converted venous blood into arterial—was bound to result in the right interpretation of the phenomena of combustion, when the observations which had led to it were sufficiently extended. Mayow's early death in 1679 was perhaps the reason why this did not occur, the development of the new chemistry being greatly retarded as a result.

Two members of the French Academy became prominent at this period, Lemery and Homberg. Wilhelm Homberg (1652-1715) was a lawyer, but gave up the practice of his profession to study natural science and medicine. He knew both Boyle and Kunckel, and was a good observer and skilful in carrying out his experiments, but a poor interpreter of results. He was tram-

mceled by alchemistic views, maintained that substances consisted of mercury, sulphur, and salt, and took little part in establishing the new theories. He contributed a large number of papers on chemical, zoölogical, botanical, and physical subjects to the French Academy.

Nicolas Lemery (1645-1715) was especially renowned as a teacher, tho he was also a good worker, dealing in the practical rather than the theoretical. His son, Ludwig Lemery, was also a distinguished chemist. The elder Lemery's greatest work was the writing of his text-book of chemistry, '*Cours de Chimie*' (1675), which embraced all that was known of chemistry, and endeavored to give a suitable connection between the facts recorded, and to systematize them. This was for many years the best text-book on the science, and was issued in thirty-two editions. Thirteen editions appeared during the author's lifetime, and a last much-changed one was issued by Baron in 1756.

Two German contemporaries of Boyle were Johann Kunckel and Johann Joachim Becher. Kunckel was essentially an experimentalist; he was imbued with a belief in the Philosopher's Stone, and regarded mercury as the necessary component of a metal. He was born at Rendsburg in 1630, and died in 1702. He was the son of an alchemist, and himself passed much of his life as the employee of sundry German princes (among them the Elector John George of Saxony, the great Elector of Brandenburg, and the Dukes of Lauenburg) in the unsuccessful pursuit of the Philosopher's Stone.

Before the second half of the seventeenth century the blowpipe had been used neither in chemical analysis nor for working glass. It was Kunckel's task to demonstrate the ease with which a metallic calx might be reduced by heating it on charcoal before the blowpipe, and to institute a more expeditious mode of hermetic sealing than that of inserting the drawn-out neck of flask or other vessel in a hot fire, hitherto in vogue.

Kunckel was the first to recognize an analogy between putrefaction and fermentation, and to show how the production of vinegar in the latter process depended on the initial formation of alcohol and avoidance of low tem-

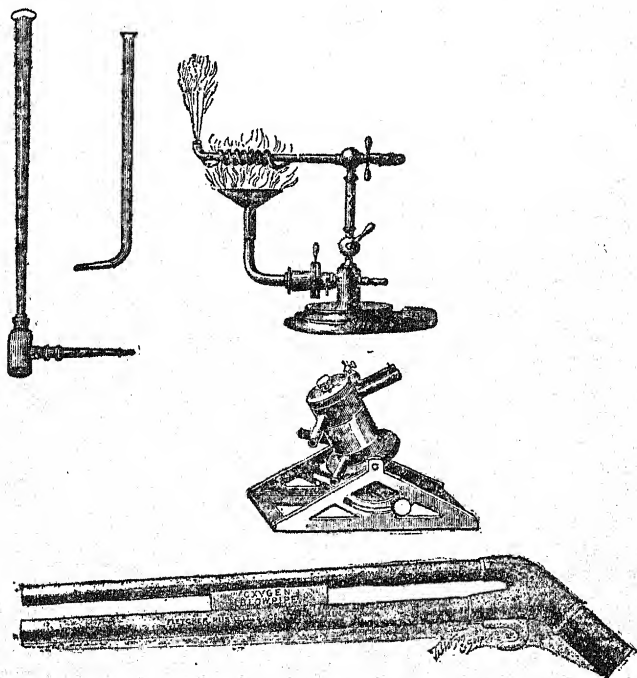


Fig. 17 —MODERN FORMS OF BLOWPIPES.

perature or presence of acids. Among his treatises the following may be mentioned: 'Oeffentliche Zuschrift von dem Phosphoro mirabili und dessen deuchtenden Wunder-Pilulen' (1678); 'Ars Vitrarya Experimentalis' (1689); and 'Philosophia chemica experimentis confirmata' (1694).

Johann Joachim Becher, who was born at Speyer in 1635 and died in London in 1682, worked almost contemporaneously with Kunckel, altho more for the theoretical explanation of already observed facts than for the practical side of the subject; but in his unsettled life and his inclination toward new schemes, he resembled the latter. He worked as an alchemist at the courts in Mainz, Munich and Vienna, but he was too honorable to deceive his patrons, and entirely too candid to allow of his remaining long in any one place. In theoretical questions as to the composition of substances, Becher attempted to revive the old ideas of Paracelsus in another form. In place of mercury, sulphur and salt, he adopted three "earths," of which all inorganic ("Subterrestrial") bodies should consist, viz., the "mercurial," the "vitreous," and the "combustible" ('terra pinguis'). The nature of any material depended upon the proportions in which these three fundamental earths were contained in it. Of especial importance was Becher's assumption that when substances were burnt or metals calcined, the 'terra pinguis' escaped: "Fire dissolves and breaks up all things made up of different parts—in metals the more volatile part is expelled." That is, he regarded combustion as a destruction. Hence, he concluded that every combustible substance must in itself contain the cause of combustibility, and that a substance incapable of being resolved into others (an element) cannot burn. It was from this conception that Stahl's phlogiston theory originated.

These theoretical views are to be found in Becher's first work, '*Physica Subterranea*' (1669), and in his last, '*Theses Chymicæ*' (1682). His doctrines acquired great celebrity through Stahl, whose work belongs for the most part to the eighteenth century, on which he conferred a character of its own by his development of the phlogiston theory.

## CHAPTER VII

### THE PHLOGISTIC PERIOD PROPER

ONE of the most interesting chapters in the history of chemical science is that dealing with the study of the phenomena of combustion and their interpretations. As Freund observes, it lends itself specially well to the purpose of indicating within the scope of not too complicated phenomena, "how a theory arises, how it is applied, how the conservatism inherent in the human mind is reluctant to give up an accustomed interpretation of nature, even when it no longer answers to the first requirements of a theory; that is, when it no longer explains the facts and laws observed in the class of phenomena to which it refers; but how after all facts are and always must be strongest, and hence how a theory is finally given up when no longer able to deal with the facts, and how its place is then taken by another better fitted to do so."

The effect of heat on matter had from early times been a subject for observation and experiment, which soon led to classification and generalization. It was observed that while some substances are not permanently changed when heated (sand, noble metals, etc.), others are (wood, sulphur, base metals, etc.). The burning of substances—that is the occurrence of a permanent change marked by the appearance of flame—great evolution of light and heat, and the remaining behind of ash—naturally arrested attention and the view that substances were combustible in virtue of the common presence in them of "fire matter" goes

back to the time of the Greek philosophers. That the substances left behind when wood is burnt or when metals such as copper and lead are heated, were alike called "cineres" (ashes), bears witness to the fact that even then these two phenomena, outwardly not very similar, the burning of wood and the change produced by heating metals, were already classed together.

The name of "calces" (Latin *calx* = lime) for burnt metals, which up to about 1600 was used along with "cineres," and after that exclusively, is due to the Arabian alchemists, and suggests an analogy with the burning of chalk, the burnt metal being produced from the metal by the same process as quick-lime from chalk, namely, by heating. All through the Middle Ages the idea was retained that what occurs when substances burn with flame, and when metals are changed to calces, is of essentially the same nature and must therefore be explained by the same cause. For many centuries sulphur was looked upon as the principle of combustibility and metals which could be "burnt"—*i.e.*, calcined—owed this to the common presence in them of sulphur. Thus, "Ubi ignis et calor, ibi sulphur," summed up this view. Becher's 'terra pinguis' had much in common with the fire of the schoolmen and the sulphur of Abertus Magnus and Paracelsus. The scope of the phenomena to which this explanation of combustion applied was extended by Stahl, and the theory of the phenomena of combustion and other analogous processes which were to be explained by the assumption of the hypothetical phlogiston was the point round which chemists in general gravitated during the eighteenth century; until the appearance of Lavoisier the phlogiston theory received the assent of most investigators.

Georg Ernst Stahl, born at Anspach in 1660, devoted himself to the study of medicine and acquired, first at Jena and later on at Halle—to which university he had been called as professor of medicine and chemistry in 1693—the reputation of a distinguished physician and academic



teacher. When he was appointed physician to the king in 1716, he removed to Berlin, where he successfully strove for the extension of chemical knowledge until his death in 1734. He investigated chemical problems in the true scientific spirit; himself guided by the ardent desire to discover the truth, he was able to draw around him pupils animated by a similar purpose. The most eminent among the Berlin chemists of the succeeding generation studied under him.

Even in his own lifetime the doctrines which he taught, together with a number of valuable detached observations, were widely disseminated by means of his writings and especially by his lectures, the later of which were published by several of his pupils. Stahl, however, exercised his greatest influence both upon his contemporaries and upon the succeeding generation by his phlogiston theory, which eclipsed all his other chemical work.

Phlogiston was defined by Stahl as "*materia aut principium ignis, non ipse ignis*," and was conceived to be "a very subtle matter, capable of penetrating the most dense substances; it neither burns, nor glows, nor is visible; it is agitated by an igneous motion ('*igneo motu*'), and it is capable of communicating its motion to material particles apt to receive it. The particles when endued with this rapid motion constitute visible fire. . . . The igneous motion is '*gyratorius seu vorticillaris*.' . . . Heat is an intestine motion of the particles of matter."

Phlogiston was a new name for an old principle. We know that the idea of the existence of a subtle fire innate in matter has pervaded physical philosophy from the earliest times. Phlogiston was, as Rodwell notes, another name for the 'pure fire' of Zoroaster; the *ατεκνεον πυρ* of Zeno; the '*subtilis ignis*' of Lucretius; the 'elemental fire,' 'astral fire,' 'sulphur,' or 'sulphureous principle' of the chemists; the '*calor cælestis*' of Cardanus; the 'sideric sulphur' of Paracelsus; the '*materia cælestis*' of Descartes, and the '*terra inflammabilis*' of Becher. The functions of this entity had been varied by different thinkers, almost as much as



its name, until Descartes gave them accurate definition. The theory of phlogiston was the theory of the 'Materia Cælestis' extended in a chemical direction. Phlogistic chemistry was Cartesian chemistry. Descartes defined the physical functions of the 'Materia Cælestis,' while Becher and Stahl defined its chemical functions and applied them to the explanation of diverse chemical phenomena. Throughout the writings of Becher and Stahl we find a sprinkling of Cartesianism; they did not, however, adopt the system in its entirety, but appear to have discarded the second and third elements, and adopted the first as the parent of their own system.

The theory of phlogiston was essentially and completely a syncretistic theory. It was built up, as Rodwell observes, of 'idola theatri,' collected from various sources, and these were cemented together by the particular 'idola specus' of Becher and Stahl. In this process of syncretism the merit of these men lay; their fault was a too hasty generalization. In that stage of chemistry syncretism was inevitable; indeed, all theories are more or less tainted by it, with the exception of those which emanate from a new mode of experimenting, such, for example, as Kirchhoff's theory of the constitution of the sun. A theory proceeds by slow evolution until it dominates or is destroyed, and it was thus with the theory of phlogiston.

Arising under the most favorable conditions, it attained full development, became most cardinal, most sovereign, and then fell. For twenty-eight years it was looking a half-formed thing through the mists of chemistry; for thirty-four years it was growing in strength and proclaiming its dynasty; for fifty-four years it was dominant, and it was fully ten years yielding up the ghost. Becher and Stahl were the prophets of a new mode of chemical thought, essentially classificatory, systematic, and syncretistic. In their day chemistry was at the commencement of a period of transition, and they bridged the gap which existed between empirical chemistry and modern chemis-

try. They did not collect the materials for the structure—they did not altogether construct it, but they designed it, and helped in the work of building. Altho a bad bridge, and built upon shifting sands, yet it was a channel of escape from mystic science, and many passed over to take refuge on the other side.

To Stahl, however, belongs the merit of grouping together the phenomena of oxidation and reduction, as we now term these, albeit by the aid of a false hypothesis. The addition of phlogiston is equivalent to reduction and its withdrawal or escape to oxidation. The analogy between respiration and the decomposition of animal matters on the one hand and combustion on the other did not escape Stahl, who likewise assigned the chief rôle in these processes to phlogiston.

The value of his theory lay therefore in the interpretation which it afforded of a variety of processes from one common point of view. The simplicity of this explanation blinded both himself and the generation which followed him to such a degree that they left unnoticed all the glaring contradictions between many actual facts and the phlogistic doctrine. Notwithstanding this, however, the latter was not an obstacle to the development of chemistry, considering that chemists like Black, Cavendish, Marggraf, Scheele, Bergman, and Priestley, who so greatly extended the science by their wide-reaching discoveries, were phlogistonists in the full sense of the word.

Stahl's two most famous contemporaries were Friedrich Hoffmann and Hermann Boerhaave. Hoffmann, born at Halle in 1660, after acquiring a thoro knowledge of medicine, mathematics and the natural sciences, practised first as a physician and then became professor of the science of medicine in Halle, where he ultimately died in 1742, after an interregnum spent in Berlin. His most important work was done in medicine, and in pharmaceutical and analytical chemistry. He combated with success the iatro-

chemical doctrines of Sylvius and Tachenius, which still held their ground with many physicians, exposing their absurdities and showing to what nonsensical deductions such exaggerations led.

Hoffmann's views on combustion were very similar to those of Stahl. With respect to the calcination of the metals and the reduction of their oxides, however, he expressed opinions which approximate to those held at the present day, believing, as he did, that metallic 'calces' contained a 'sal acidum' in addition to a metal, the former of which escaped when the 'calces' were reduced. This assumption did away with the similarity between combustion and calcination; these phenomena became indeed rather opposed to one another thereby, and with this the special use of the phlogiston theory vanished. Hoffmann was a very voluminous author, and his collected works in six volumes and five supplements, entitled '*Opera Omnia Physico-medica*' (1740-1760), show clearness of style and precision of expression. Gmelin in his '*Geschichte der Chemie*' enumerates 122 chemical treatises by Hoffmann.

Hermann Boerhaave was born at Voorhout, near Leyden, in 1668, where he received his education and became professor of medicine and afterward of chemistry and botany. The thirty-six years of his residence there were the most brilliant in the history of this university. Looking at his chemical work alone, he is found distinguished in the main as a teacher and for his skill in interpreting chemical facts and the clearness of his theoretical views. He exposed the errors of the iatro-chemists and recognised chemistry as a distinct science.

He also showed the falsity of the views held by the alchemists. He spoke only of things tested and observed by himself, and spared neither pains nor time to have his observations correct. For instance, the alchemists maintained that mercury could be fixed in the form of a fire-proof metal, without the addition of any other substance. Boerhaave kept mercury at a somewhat raised tempera-

ture in an open vessel for fifteen years without noting any change. So, too, when heated higher in a closed vessel for six months no change could be discovered. This convinced him that the fixing of mercury was an impossibility. The alchemists said also that if mercury was repeatedly distilled, a more volatile essence with peculiar properties could be obtained. Boerhaave carried out this distillation five hundred times without securing the essence. And so he tested other of their peculiar notions and prescribed methods without obtaining the results promised; and as the methods were still credited in some quarters, he did good service in disproving them, and won for himself the reputation of being a most excellent and painstaking worker.

His lectures were published first in the 'surreptitious edition,' *Institutiones et Experimenta Chemiæ* (1724) and afterward corrected by him under the title *Elementa Chemiæ* (1732). Eleven editions and translations were published in Germany, France, and England.

Boerhaave appears to have concurred in the phlogiston theory in many points. At least he expressed no opinions contrary to Stahl's fundamental views, altho he did not agree in regarding the 'calces' of the metals as the earthy elements of these latter.

The influence of Stahl's doctrine manifested itself more immediately in Germany, where it received the almost unequivocal support of chemists, Berlin remaining the center point of this theory. Among the men who upheld and endeavored to propagate it, Marggraf was the most active.

Kaspar Neumann (born 1683) and Johann Theodor Eller (born 1689), contemporaries of Stahl, were also active adherents of the doctrine in Berlin. Both of them, as professors at the Medico-Chirurgical Institute, were in a high degree active in maintaining and disseminating a knowledge of chemistry. Their own observations were, however, of little importance; Neumann made the first

accurate observation of the acid obtained from ants; and the views of Eller were chiefly upon subjects of medical physiology, and are full of crude speculations. Stahl's pupil, Johann Heinrich Pott (born 1692), improved chemistry by many valuable observations, but he was unfortunate in his explanation of these. He regarded boracic acid, for instance—a substance which he had himself investigated carefully—as consisting of copper vitriol and borax. The results which he achieved were not, as von Meyer notes, at all commensurate with his untiring perseverance, which he showed, among other ways, in his endeavors to prepare porcelain. Altho an adherent of the phlogistic doctrine, Pott did not bring forward anything new in its favor; with regard to the nature of phlogiston itself, he could only express the opinion that it was "a variety of sulphur." A notable achievement associated with his name was a wide extension of the method of dry analysis. His 'Chymische Untersuchungen' was published in Berlin in three parts in 1757.

Neumann's pupil, Marggraf, was the last of the well-known German chemists of the phlogiston period. Andreas Sigismund Marggraf was born at Berlin in 1709, and proved a most able experimenter; indeed, it is for his many isolated discoveries that he is remembered rather than for any influence exerted on the general trend of chemical philosophy. One of the most lasting benefits owed to him is the introduction of the microscope as an aid in laboratory work. The occasion was noteworthy. A paper appeared in the memoirs of the Berlin Academy for 1745, in which Marggraf stated that small crystals of sugar might be seen with the aid of a microscope upon the finely divided and desiccated roots of the carrot and beetroot. He further stated that this sugar could be extracted by lixiviation with hot alcohol, and added that mere compression of carrot or beet would yield a saccharine liquid, from which the sugar might readily be extracted. These observations remained unnoticed, un-

til the continental blockade of France in 1806 urged its people to find some substitute for their imported sugar.

Of prime importance was Marggraf's observations on phosphoric acid, whose principal physical and chemical properties he accurately described. He obtained this acid by burning ordinary phosphorus in the air, and dissolving the resulting "fleurs de phosphore" in water; also by heating phosphorus with concentrated nitric acid. Marggraf's work on the composition of gypsum was remarkable; he had noticed that potassium sulphate on heating with charcoal emitted the pungent smell of burning sulphur, and as this also occurred when gypsum or heavy spar was substituted for the potassium salt, they too must be compounds of sulphuric acid. One should not forget his introduction of potassium ferrocyanide as a reagent for iron, nor his separation of microcosmic salt from urine; he remarked that it was this salt which contained the phosphorus.

With great talent for observation Marggraf united the gift of deducing what were generally sound conclusions from his work. In one point, however, Marggraf, like all phlogistonists, was not in a position to do this; altho he had himself proved that phosphorus increases in weight by conversion into phosphoric acid, he could not free himself from the idea that phlogiston escaped during this process of combustion. And he could never be brought to see that this conception was an erroneous one, altho the anti-phlogistic doctrine was brought out several years before his death. Marggraf's papers are, as mentioned, almost all contained in the 'Memoirs' of the Berlin Academy; most of them were published from 1761-1767 in two volumes, under the title 'Chymische Schriften.' A French edition appeared in 1762.

In France, the principal exponents of chemistry during the eighteenth century, until the downfall of the phlogistic system, were Geoffroy, Duhamel du Monceau, Rouelle and Peter Joseph Macquer.



Stephen François Geoffroy (the elder, to distinguish him from his less celebrated younger brother, Claude Joseph, whose work was chiefly pharmaceutico-chemical) was born in Paris in 1672, and helped for some time in his father's apothecary shop; he gave himself up, however, to chemical and medical studies, and labored with great success as professor of medicine in the Jardin des Plantes from the year 1712 until his death in 1731. Geoffroy became well known throughout the scientific world by his researches upon chemical affinity; his 'Tables des Rapports' (tables of affinity), in which the results of his most important observations are collected, exercised a great influence upon the doctrine of affinity. His theoretical views were less idoneous—*e.g.*, he looked upon the iron found in the ashes of plants as having been produced artificially during the process of ignition.

Geoffroy's views on combustion were in principle those of Stahl, though he expressed himself in the nomenclature of the earlier period; yet there was much promise in his conviction that the different 'calces' were radically different bodies.

A real service was rendered by him by the energy with which he attacked alchemistic frauds, subjecting these as he did to critical examination in the memoir 'Des Supercheries concernant la Pierre Philosophale,' presented to the French Academy. Geoffroy's treatises were published partly in the 'Memoirs of the French Academy,' and partly in the 'Philosophical Transactions.' His long-celebrated work, 'Tractatus de Materia Medica,' shows that he regarded chemistry as a sister science and an invaluable aid to medicine.

Henri Louis Duhamel du Monceau (born 1700, died 1781), of the school of Lemery and Geoffroy, spent his life in Paris, where his versatility gained for him a high reputation. His sterling work was not by any means in pure chemistry alone, but also in physics, meteorology,



physiology, botany, and particularly in chemistry as applied to agriculture.

Duhamel's great achievement was the differentiation of the two alkalis, soda and potash. The composition of ordinary salt had hitherto eluded research. Stahl, it is true, believed one constituent to be an alkali, and an alkali quite different from potash, if one might judge by differences in the crystalline form and solubilities of their respective salts. There was a vagueness about his work, however, and it had met with little recognition. Duhamel published a paper in 1736 on sea salt which put the matter beyond question. In it he first showed that the base of salt was not an earth, for the addition of potash caused no precipitation, then that its several salts all differed essentially from those of potash corresponding. He laid stress, too, on the fact that the further one moves from the sea, the less the quantity of the new base and the greater the quantity of potash in the surrounding vegetation. Subsequently, while describing minutely the differences between the analogous salts of these bases, Duhamel mentioned the yellow and violet colorations which they respectively give to a colorless flame.

While Duhamel worked mainly as an academician, Guillaume François Rouelle (born 1703, died 1770) was occupied in teaching at the Jardin des Plantes, and some of his pupils, particularly Lavoisier and Proust, attained the highest eminence. At the same time he was also busy as an investigator, as many admirable observations and conclusions drawn from the latter show. Rouelle fixed the meaning of the term "salt" (in the 'Memoirs' of the Academy for 1745) from a far more general point of view than van Helmont or Tachenius had done. The composition of a substance alone was sufficient to tell him whether it belonged to the class of salts or not. Salts were produced by the combination of acids of every kind with the most various bases; and in addition to neutral salts, he drew a distinction between acid and basic ones.

With views so lucid as these, Rouelle was far ahead of his contemporaries.

Rouelle's "Cours de Chimie," according to Hoefer, exists only in manuscript.

The last of the French chemists of renown to adhere to the phlogistic theory was Pierre Joseph Macquer, who was born at Paris in 1718. He became a member of the French Academy at the age of twenty-seven. Excellent opportunity for work was afforded him by his position as professor at the Jardin des Plantes, and his methods of research were more like those of the present. He determined the solubility of various salts in alcohol, and used this as a means of separating them from one another. Some of his researches were on potassium arseniate, and on the coloring matter of Berlin blue. The later he identified with phlogiston because it was destroyed on heating. He was the author of several text-books, "Elemens de Chymie Theorique" (1749) and "Elemens de Chymie Pratique" (1751), which were highly thought of; but his chief work was his "Dictionnaire de Chymie," which appeared first in 1766. This was the first dictionary of chemistry, and it was enlarged three times, and translated into English, German, Italian and Danish. Macquer died in 1784. All his life he remained a phlogistonist, and did all that he could to reconcile the continually augmenting dissidences between theory and facts; he paid no attention to proportions by weight, for it was only in this way that he could maintain the phlogistic hypothesis. And even although it was proved to be erroneous and untenable several years before his death, he was still unable to relinquish it.

During the eighteenth century many distinguished chemists flourished in Great Britain and Sweden, all of whom were adherents to the phlogiston theory of Stahl, and this notwithstanding the fact that it was their investigations, particularly those of Black, Cavendish, Priest-

ley, Scheele, and Bergman, which destroyed the foundations of this theory.

Black was born near Bordeaux in 1728, and died in Edinburgh in 1799. His father, a wine-merchant, was originally a native of Belfast, being descended from a Scotch family which had been settled there for some time. Black's original thesis for his degree was entitled 'Experiments upon Magnesia Alba, Quicklime, and other Alcaline Substances.' It was published in 1755, and was reprinted in 1777 and 1782. During the ten years he was Professor of Medicine at the University of Glasgow he began and made great progress with his well-known researches on the heat of fusion of ice, and the heat of vaporization of water, or, as he termed them, the "latent heats" of water and of steam.

The carbonates of the alkaline earths were before Black's time regarded as simple substances; and it was also supposed that when limestone was burnt fire-stuff was taken up, and that this went over into potashes or soda when these were causticized by means of lime. Black, on the other hand, showed by his investigations that when limestone (carbonate of lime) or "Magnesia alba" was calcined, something escaped which caused a loss of weight and which was identical with van Helmont's "gas sylvestre." This gas—which he termed "fixed air" on account of its being held bound by caustic alkalies, lime, etc.—he proved to be also present in the mild alkalies; and these latter became caustic when deprived of their carbonic acid by lime or magnesia. In this research methods are met with which have the imprint of a new departure. That Black devoted great attention to the proportions by weight of the compounds which entered into the reaction is seen in all his investigations; and it is thus easy to understand how he gave up the phlogiston theory and concurred in the doctrine of Lavoisier when the correct explanation of combustion and similar processes became possible through the discovery of oxygen.

Cavendish, the distinguished co-worker and fellow countryman of Black, was born at Nice in 1731, two years before Priestley; but, notwithstanding his brilliant circumstances, he lived the life of a recluse, devoting himself entirely to the furtherance of his beloved science. He died in 1810. His most important work was the discovery of hydrogen, which he called "inflammable air." This he distinguished from the "fixed air" of Black, concluding that this "inflammable air" was the unaltered phlogiston of the metals. He was the first to attempt to determine the specific gravity of the gases. He showed that lime carbonate was held in solution in water by dissolved fixed air or carbonic acid. He proved in his experiments on air that when hydrogen was burned water was formed, thus really determining the composition of water, tho he did not recognize this fact. This led to a sharp controversy as to the phlogistication of the air or atmosphere, and in the hands of that great interpreter of results, Lavoisier, did much to clear up and advance chemical theory.

The opposition of Cavendish to the antiphlogistic doctrine, which he helped to found by his own investigations, can only be explained by the fact that he did not take the proportions by weight in the processes of combustion into due consideration, but interpreted the latter in a manner which appeared to him sufficiently convincing, viz., by regarding hydrogen, "inflammable air," as identical with phlogiston.

In addition to this Cavendish showed a wonderful exactitude in his researches upon gases, whose specific gravities and volume-ratios in chemical reactions he established. With what ingenuity he thought out and carried through physical experiments is well illustrated in his work on the specific heats of metals, and in his attempt—the first one which was successful—to determine the specific gravity of the earth. Another instance will be fresh in the memory of most readers, viz., Cavendish's suspicion, from the results of his own experiments on the combina-

tion of oxygen and nitrogen, that there was possibly still another gas present in the air in small quantity (argon). When this marvelous versatility is considered and the thoro mathematical training that Cavendish had gone through is remembered, the wonder seems great that he laid too little stress upon proportions by weight in chemical reactions.

Joseph Priestley was born at Fieldheads, near Leeds, in 1733, and received his education at a public school and at an academy of the Dissenters. His studies were theological in character, and he became a dissenting minister. He was not a success in this work, becoming extremely unpopular even with his own sect. He also conducted a school, but was in very needy circumstances. He was able, however, to buy a few books and some instruments, including a small air-pump, an electrical machine, etc., and was tireless in his work, training himself and his scholars in natural science. Meeting Franklin in London, he was attracted to the study of electricity, and wrote a history of electricity. This, together with some new experiments on electricity performed by him, won some outside reputation and his election as Fellow of the Royal Society.

He moved to Leeds, settling near a brewery. This gave him opportunity for examining the "fixed air" discovered by Black, and which had been shown to be one of the products of fermentation. He collected this gas from the vats, and performed many experiments with it. Moving away from the brewery, he had to prepare the "fixed air" for himself; and this led to his devising the simple and useful pneumatic trough. In the heated times of the French Revolution, his church and dwelling-house were mobbed and burned, his library and apparatus destroyed, and he himself escaped with difficulty to London, and finally took refuge in America, where he settled in Pennsylvania. In this country he pursued his scientific experiments, discovering carbon monoxide. He died in retirement in the

year 1804. One French historian, Henri Gautier, states in his "Essai sur l'histoire de la Chimie" that Priestley "sought an asylum among the Indians, and eventually he and his entire family died by poison!"

Priestley was a brilliant investigator, performing many most striking experiments. He was, however, neither thoro nor very careful, and was lacking in the scientific acumen needed for the proper interpretation of his results. It was upon the gases that his most valuable work was done; his invention of the pneumatic trough enabling him not only to discover new gases, but to investigate the properties of many already partially known. He considered that "More is owing to what we call chance . . . than to any proper design or preconceived theory in this business," and shows how large a share this element of chance had in his discovery of the new gas, oxygen.

His method of experimenting is well illustrated by his own account of his discovery of oxygen (1774): "Having procured a (burning) lens, I proceeded with great alacrity to examine, by the help of it, what kind of air a great variety of substances would yield, putting them into vessels filled with quicksilver, and kept inverted in a basin of the same. After a variety of other experiments, I endeavored to extract air from 'mercurius calcinatus per se,' and I presently found that, by means of this lens, air was expelled from it very readily. Having got about three or four times as much as the bulk of my materials, I admitted water to it, and found that it was not imbibed by it. But what surprised me more than I can well express, was that a candle burned in this air with a remarkably vigorous flame. I was utterly at a loss how to account for it." His experiments showed him that this air "had all the properties of common air, only in much greater perfection"; and he called it "dephlogisticated air," regarding it simply as very pure ordinary air. In 1843, Cuvier endeavored to show that the French chemist Bayen preceded Priestley in the discovery of oxygen. Bayen, however, in



reducing "precipitate per se," noted only the metal and entirely disregarded the escaping gas.

He seems to have looked upon all gases as easily changeable, one into the other, at least in the first period of his work. Many experiments were made by him on the action of the various gases known to him upon animals and plants. He would place a mouse in a jar of the gas, and notice the effect upon its breathing and general life processes. Plants were grown in similar jars, and the result upon the growth noted. He showed that air which had become noxious through breathing or the burning of a candle could be restored to its original condition by growing a plant in it. This, he said, was due to the impregnation with phlogiston in the first case, and its removal in the second. "It is very probable," he wrote, "that the injury which is continually done to the atmosphere by the respiration of such a number of animals as breathe it, and the putrefaction of such vast masses, both of vegetable and animal substances exposed to it, is, in part at least, repaired by the vegetable creation." He was unable to explain how this was accomplished.

He held that all combustible bodies contained hydrogen. This was, in his view, phlogiston. The metals contained it, and their "calces," or oxides, were simply the metals deprived of hydrogen. Thus, he showed that when iron oxide was heated in hydrogen gas the hydrogen was absorbed and metallic iron formed. Rich iron slag or cinder was, in his opinion, iron with some hydrogen retained. To prove this, it was mixed with the carbonates of the alkaline earths and heated strongly. This gave him an inflammable gas, and all inflammable gases were hydrogen in a more or less impure condition, according to his belief.

That water could be impregnated with carbon dioxide was found out by him, and its use in disease suggested. Nitrogen dioxide and carbon monoxide were discovered by him, but his greatest discovery was that of oxygen gas. He examined sulphur dioxide, hydrochloric acid, and am-



monia in the gaseous form. These are only the most important of his discoveries. Inaccurate in his experiments, he was decidedly weak as a theorizer. He was a firm believer in the phlogiston theory, and endeavored to explain the various phenomena noted by him by means of it.

The important works of Priestley are the following: 'Directions for impregnating Water with Fixed Air in order to communicate to it the peculiar spirit and virtues of Pyrmont Water, and other mineral waters of a similar nature' (1772); 'Philosophical Empiricism' (1775); 'Experiments and Observations on Different Kinds of Air' (1774-1779); 'Experiments and Observations relating to various branches of Natural Philosophy with a continuation of the Observations on Air' (1779-1786); and 'Experiments on the Generation of Air from Water' (1793).

Coetaneously with the three last-mentioned British chemists, two eminent investigators, Torbern Olaf Bergman and Karl Wilhelm Scheele, were supporting the phlogistic theory in Sweden, but their brilliant discoveries and observations only served so deeply to undermine it that its dispensation was inevitable. Bergman had acquired such a wide knowledge of the natural sciences that he taught with eminent success as professor of physics, mineralogy and chemistry at Upsala. He was born in the year 1735, and died at the early age of forty-nine, undoubtedly from the effects of overwork upon a weak constitution. His chief services to chemistry, to which from 1767 he mainly devoted himself, were in the domain of analysis, which he treated systematically and enriched by valuable methods.

Bergman's system of wet analysis first took form during an investigation of natural waters; but he later made it embrace the examination of minerals in general, fusing such of these as were insoluble in hydrochloric acid with carbonate of potash. Bergman laid great stress on the analytical value of the blowpipe, between whose inner and outer flame he discriminated; and he endeavored to extend

the use of such reagents as soda, borax, and microcosmic salt, substances whose value had been demonstrated by the mineralogist Cronstedt. It is to Bergman's pupil Gahn that the introduction of cobalt solution as a reagent is owed, and the substitution of platinum wire for the gold or silver used hitherto. Up to this time, reduction to the metallic state had been regarded as a necessary precedent to the quantitative estimation of metals in combination. Bergman now introduced the revolutionary method of combining them in stable salts of known composition, and from the weight of these calculating the metallic content.

Bergman's analyses were not very accurate, yet they enjoyed the widest popularity; on the other hand, his German contemporary, Carl Friedrich Wenzel, found little consideration, tho his method was similar, and his results more fortunate. Meanwhile, the number of chemists who applied themselves to the quantitative side of phenomena was steadily increasing, an indication of the straits to which the phlogiston theory had been reduced. Yet at this eleventh hour Bergman set to work to determine the relative quantities of phlogiston in metals. Believing that metals only dissolve after conversion into their 'calces,' he ascertained those weights of various metals which precipitated the same weight of some other in solution, surrendering their phlogiston to its 'calx'; these weights, to his mind, contained the same quantity of phlogiston.

He knew well how to render his chemical experiences useful for the definition and classification of minerals, and thereby laid the foundation of mineralogical chemistry and chemical geology. The current views upon chemical affinity gained through him precision and clearness; the scientific character of chemistry was materially raised by such observations, and a general survey of chemical processes rendered much easier. His papers appeared originally in the "Memoirs" of the Academies of Stock-

holm and Upsala; later on they were collected together and published in six volumes in 1779-1790, under the title 'Opuscula Physica et Chemica.' This Latin edition was translated into English in 1784-1791.

Carl Wilhelm Scheele was born in 1742 in Stralsund, the capital of Swedish Pomerania, where his father was a merchant and a burgess. He was the seventh of eleven children. After receiving his education, partly in a private school, partly in the public school ("gymnasium") at Stralsund, he was apprenticed at the age of fourteen to the apothecary Bauch in Gothenburg. In those days an apothecary was in large measure a manufacturer as well as a retailer of drugs. He had to prepare his medicines in a pure state from very impure materials, as well as to mix them in order to carry out prescriptions; and, indeed, he himself often, as sometimes happens still, ventured to prescribe in mild cases. Scheele's master taught him such methods, and in addition instructed him in the use of the chemical symbols in vogue at that date; these he afterward freely employed in his manuscripts, and this renders them exceedingly difficult to decipher.

Restricted almost entirely to several old text-books, together with the fairly good chemical inventory of Bauch's shop, Scheele, by constant experimenting, acquired such a knowledge of things chemical that, by the time he went to Malmo (in 1765) he had gained more experience than the majority of the chemists of the time, altho he was yet only an apprentice. At Malmo and also in Stockholm (1768-1770) and Upsala (1770-1775), he increased his knowledge of the most important branches of chemistry without, however, becoming so well known at the time as he deserved.

It was only when, as stated by Nordenskiöld, through Gahn he came into close relation with Bergman—a connection which began in a misunderstanding and coolness, but which developed into a friendship—that Scheele continued to gain steadily in reputation. After taking over

the pharmacy at Koping in 1775, he was able to devote himself more closely to scientific work, and with still more brilliant results. The records of his researches followed one another rapidly in the 'Transactions of the Stockholm Academy, into which he had been received as "Studiosus Pharmacizæ" in 1775. In 1777 he published the results of his investigation on air, oxygen, combustion and respiration at Upsala and Leipzig in a volume entitled 'Chemische Abhandlung von der Luft und dem Feuer' ('A Chemical Essay on Air and Fire'). After his early death at barely forty-four years of age, his collected works were published in two volumes in German by S. F. Hermbstädt (Berlin, 1793), under the title 'Sämmtliche Physische und Chemische Werke.' The Latin edition by Schaefer had appeared four years previous.

Altho the results of his principal investigations will be discussed further on, it is important to mention here that to Scheele is due the first knowledge of chlorine and of the individuality of manganese and baryta. He was an independent discoverer of oxygen, ammonia and hydrochloric acid gas. He discovered also hydrofluoric, nitro-sulphonic, molybdic, tungstic, and arsenic acids among the inorganic acids; and oxalic, citric, tartaric, malic and mucic among the organic acids. He isolated glycerin and milk-sugar; determined the nature of microcosmic salt, borax, and 'Prussian blue,' and prepared hydrocyanic acid. He demonstrated that plumbago is nothing but carbon associated with more or less iron, and that the black powder left on solution of cast iron in mineral acids is essentially the same substance. He ascertained the chemical nature of sulphuretted hydrogen, discovered arsenuretted hydrogen, and the green arsenical pigment which is associated with his name. He found new processes for preparing gallic acid, ether, powder of algaroth, phosphorus, calomel, and 'magnesia alba.' His services to quantitative chemistry included the discovery of ferrous ammonium sulphate, and of the methods still in use for

the analytical separation of iron and manganese, and for the decomposition of mineral silicates by fusion with alkaline carbonates.

The greatest work of the life of Scheele, however, was his memoir on 'Air and Fire,' which appeared in 1777, and which, on account of its relations to the chemical theory of that time, attracted universal attention, and was translated into English, French and German. The chief part of the experimental material for this work, as is proved by the correspondence and laboratory journals published in 1892 by Nordenskiöld, was collected partly in Malmo and Stockholm—that is, before the autumn of 1770, and partly during the earlier portion of his stay in Upsala—that is, prior to 1773. These dates are important in view of Scheele's relations as a discoverer to Priestley and Lavoisier. A number of circumstances, and more especially the dilatoriness of the publisher Swederus, retarded the appearance of the book. From the letters to Gahn it appears that the manuscript was sent to the printer toward the close of 1775, but nearly two years elapsed before the work was made public. Scheele, in several of his letters, laments over the delay.

In August, 1776, he wrote to Bergman: "I have thought for some time back, and I am now more than ever convinced, that the greater number of my laborious experiments on fire will be repeated, possibly in a somewhat different manner, by others, and that their work will be published sooner than my own, which is concerned also with air. It will then be said that my experiments are taken, it may be in a slightly altered form, from their writings. I have to thank Swederus for all this." However, no imputation of plagiarism was ever brought against Scheele. The whole conduct of his life was proof indeed against even a suspicion of unfair dealing. He was exceedingly unselfish and veracious. To quote Thorpe, "With all Priestley's candor and sense of rectitude, he had Cavendish's indifference to fame and his contempt for notoriety.

It can hardly be doubted, however, that had Scheele's work appeared in 1775 he himself would have occupied a still higher position in the estimation of his contemporaries, and that it would not have been left to posterity to assign him his true place in the history of scientific discovery." He further expresses the following appreciation:

"It is impossible to read this, or indeed any other of Scheele's memoirs, without being impressed by his extraordinary insight, which at times amounted almost to divination, and by the way in which he instinctively seizes on what is essential and steers his way among the rocks and shoals of contradictory and conflicting observations.

"It is, perhaps, idle to speculate on the causes which prevented Scheele from recognising the full significance of his work. It may be that from the lack of mathematical training the quantitative aspects of chemistry had few attractions for him, but it is equally probable that the peculiar character of his inquiries may have been determined by the circumstances of his position, by his poverty, and by the want of the refined and costly apparatus needed for quantitative research. But surmises, as Scheele himself said, cannot determine anything with certainty. It must be admitted that he was wanting in the faculty of coördination, grasp of principle, and power of generalization that so strikingly characterize Lavoisier; and his greatest investigation, while it testifies to his genius as an experimentalist, reveals, no less clearly, his weakness as a theorist. But when every legitimate deduction has been made, Scheele's work, with all its shortcomings and limitations, stamps him as the greatest chemical discoverer of his age. His story constitutes, indeed, one of the most striking examples of what may be achieved by the diligent cultivation of a single natural gift."

## CHAPTER VIII

### DEVELOPMENT OF SPECIAL BRANCHES DURING THE PHLOGISTIC PERIOD

ALTHO the services of the chemists whose investigations did most toward building up the chemistry of gases have been referred to, yet the influence of this work in shaping chemistry was so great that discussion of pneumatic chemistry and its relations to the phlogistic theory, in more detail, is necessary. Boyle, ingenious though he was, was unable to fathom the mystery of atmospheric air. His views regarding it are succinctly stated by him in his 'Memoirs for a General History of the Air,' and in the same work he sums up the views of the ancients. His words are:

"The Schools teach the air to be a warm and moist element, and consequently a simple and homogeneous body. Many modern philosophers have, indeed, justly given up this elementary purity in the air, yet few seem to think it a body so greatly compounded as it really appears to be. The atmosphere, they allow, is not absolutely pure, but with them it differs from true and simple air only as turbid water from clear. Our atmosphere, in my opinion, consists not wholly of purer aether, or subtile matter which is diffused thro' the universe, but in great number of numberless exhalations of the terraqueous globe; and the various materials that go to compose it, with perhaps some substantial emanations from the celestial bodies, make



up together, not a bare indetermined feculancy, but a confused aggregate of different effluvia."

His researches, however, show a marked advance over those of van Helmont in the mode in which he collected gases and worked with them; at the same time neither he nor his contemporaries felt quite sure whether carbonic acid and hydrogen, whose characteristic properties he was acquainted with, differed materially from atmospheric air. In fact, the idea that gases were simply atmospheric air with various admixtures, had become fixed in the minds of chemists. The experimentalist Stephen Hales, for example, discovered gases and prepared them in a more or less pure state, but had no theory to guide him, and concluded that it was possessed of "a chaotic nature," since he failed to recognise his gases as different kinds of matter, but regarded them all as modified air.

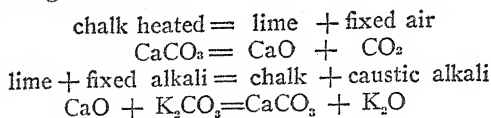
Black's account of "fixed air" and its properties is the first example of a clear and logical series of experimental researches, where nothing was taken for granted, but everything was made the subject of careful quantitative measurement. It was not long since Hales had announced air to be a chaotic mixture of effluvia. Black showed that common air contains a small amount of "fixed air," and that "fixed air" must be considered as a fluid differing in many of its properties from common air, especially in its being absorbed by quicklime and by alkalies. It must be remembered that at that time carbon was not recognised as an element; and hence, tho Black knew that "fixed air" was a product of the combustion of charcoal, he did not attribute it to the union of carbon with oxygen.

Black held that the change from chalk to lime consists only in the withdrawal of "fixed air," and he adduced in proof the changes in weight accompanying the change from chalk to lime and back again:

"A piece of perfect quicklime, made from two drams of chalk, and which weighed one dram and eight grains, was reduced to a very fine powder, and thrown into a fil-

trated mixture of an ounce of a fixed alkaline salt and two ounces of water. After a slight digestion, the powder, being well washed and dried, weighed one dram and fifty-eight grains. It was similar in every trial to a fine powder of ordinary chalk."

The changes referred to are:



The methods of collecting gases had improved considerably since the times of Hales. Air was ascertained to be a fluid capable of measurement, which possessed weight, and which could be transferred from one vessel to another, just like all other fluids. The apparatus which Black, Priestley, Bergman, and Scheele employed, and those which we use at the present time, gradually developed themselves from that of Hales. Joseph Priestley was the first to describe the collection of gases over mercury, and by this means he succeeded in discovering gaseous ammonia, hydrochloric acid, silicon fluoride, and sulphurous acid—gases which had been overlooked so long as water was employed in the collecting vessels. As mentioned before, Scheele is now known to have anticipated Priestley in the isolation of some of these gases, as well as of nitric oxide and sulphuretted hydrogen (hydrogen sulphide). These investigations, along with the recognition of Cavendish that hydrogen is a peculiar gas, and the supplemental researches of Bergman and Black on carbonic acid, are to be emphasized as being particularly noteworthy, since they helped to do away with many misconceptions and errors.

The discovery of so many gaseous substances of such different character naturally roused the chemical world. The properties of each gas were carefully studied; and, after Mayow's researches, and especially after the more

exact determinations conducted by Cavendish, the density was taken as the criterion of one gas differing from another and from atmospheric air. Due attention was also given to the greater or lesser absorption of gases by water, as a distinct test for some of them; Bergman, for instance, determined with fair accuracy the solubility of carbonic acid in water. However, the exact composition of gaseous bodies remained unknown during this period, great uncertainty prevailing even about the simplest of them, until Lavoisier had pronounced his opinion as to the elementary nature of oxygen and hydrogen. But this could not be otherwise, so long as phlogiston was believed to be present in most gases. Hydrogen was thought to be identical with phlogiston by many chemists, soon after the middle of the eighteenth century, Cavendish and Richard Kirwan setting the precedent for this; others looked upon coal as being rich in phlogiston, if not as the latter itself; and often confused opinions were expressed concerning the composition of carbonic acid, carbonic oxide, nitric oxide, sulphurous acid, sulphuretted hydrogen, and other gases, these opinions being made to conform with the views of the phlogistic doctrine prevalent at that time.

Of greater importance than these views upon the constitution of the gases just named were the long unsettled questions, "Is atmospheric air a simple or a compound body, and—if the latter—what are its constituents or ingredients?" These questions were solved experimentally by chemists belonging to the phlogistic era, more particularly by Scheele and Priestley; but it was left to Lavoisier to interpret their observations correctly.

The first observation which assisted in overthrowing the old assumption of air being a simple substance, was the deportment of an enclosed volume to a burning body and to metals heated in it. The alchemists had asserted that when a substance is burned in the air it is separated or analyzed into things simpler than itself. The acute Boyle had said the process is not necessarily a simplifica-

tion; it may be, and certainly sometimes is, the formation of something more complicated than the original substance, and when this happens, the process often consists in the fixation of 'the matter of fire' by the burning substance. He was led by his investigations in this direction to the assumption that one ingredient of the atmosphere was necessary to respiration and combustion, and that the increase in weight during the calcination of metals was due to a ponderable firestuff. He remarked that,

"It will not be irrational to conjecture that multitudes of these fiery corpuscles, getting in at the pores of the glass, may associate themselves with the parts of the mixt body whereon they work, and with them constitute new kinds of compound bodies, according as the shape, size and other affections of the parts of the dissipated body happen to dispose them. . . . I have been induced to think that the particles of an open fire working upon some bodies may really associate themselves therewith; and add to the quantity." (Boyle, 'The Sceptical Chymist,' 1661.)

He was unable to isolate this ingredient, however.

Stahl paid no attention to the change in weight resulting from calcination—a position which was taken also by many later phlogistonists, who either regarded such a change as accidental or advanced crude explanations of it. Johannes Juncker, for example, pointed out that the metallic 'calces' were denser than the metals, and consequently heavier—decidedly an incorrect statement, as Boyle had already demonstrated in certain cases that the 'calces' were specifically lighter than their corresponding metals. Equally ridiculous was the assumption that the phlogiston which escaped in calcination possessed a negative weight, and therefore that the end product was the heavier.

In 1630 Jean Rey published a series of essays entitled: 'Essays of Jean Rey, Doctor of Medicine, on the Researches of the Cause owing to which Tin and Lead increase in Weight when they are calcined.'

"Now I have made the preparations, nay, laid the foundations for my answer to the question of the sieur Brun, which is, that having placed two pounds six ounces of fine English tin in an iron vessel and heated it strongly on an open furnace for the space of six hours with continual agitation and without adding anything to it, he recovered two pounds, thirteen ounces of a white calx; which filled him at first with amazement, and with a desire to know whence the seven ounces of surplus had come. And to increase the difficulty, I say that it is necessary to enquire not only whence these seven ounces have come, but besides them what has replaced the loss of weight which occurred necessarily from the increase of volume of the tin on its conversion into calx, and from the loss of the vapours and exhalations which were given off. To this question, then, I respond and sustain proudly, resting on the foundations already laid, 'That this increase in weight comes from the air, which in the vessel has been rendered denser, heavier, and in some measure adhesive, by the vehement and long-continued heat of the furnace: which air mixes with the calx [frequent agitation aiding] and becomes attached to its most minute particles: not otherwise than water makes heavier sand which you throw into it and agitate, by moistening it and adhering to the smallest of its grains.'"

The manner in which Rey arrives at his answer is not by any direct experiments on calcination, but rather by experiments and the reference to experiments of a purely physical nature, such as the discussion of the causes, like change of volume, which can, and of those, like heat, which cannot, produce change of weight. Thus he lays a sound foundation for his method, which is one of elimination, showing that none of the causes to which it had been usual to ascribe the observed increase in weight could be considered legitimate; that it could not be due to

the giving up of heat of negative gravity, not to the absorption of fire matter of positive weight, not to an increase in density, not to the absorption of soot or of anything else from the materials of the containing vessels, And so none is left unchallenged of all the possible modes of explanation save that of the fixation of the air.

Consequently, his conclusion that calcination of a metal probably consists in the fixation of particles of air by the metal, does not amount to a proof.

Mayow assumed that a "*spiritus igno-aëreus*" brought about combustion. According to him, the substance that is being calcined lays hold of this particular constituent of the air, which, however, he failed to isolate. Nevertheless, he approached closely to the correct interpretation of the phenomena in question, the real solution of which was brought forth after oxygen and nitrogen had been prepared with success.

Nitrogen was first isolated by Scheele, but Daniel Rutherford, who discovered it independently in 1772, preceded Scheele in publication. Rutherford removed the oxygen from ordinary air by combustibles such as charcoal, phosphorus, or a candle; and having got rid of the carbon dioxide, in those cases when it was formed, by alkali or lime, he obtained a residue, now known as nitrogen. His view of the nature of this gas, in the phlogistic language of the time, was that the burning bodies had given up some of their 'phlogistic material' to the air, which was thus altered. Nitrogen was 'phlogisticated air,' even tho incombustible; hydrogen, too, was phlogisticated air, but air produced by the union of pure phlogiston with atmospheric air. The step taken by Rutherford, under Black's guidance, was an advance, though not a great one, in the development of the theory of the true nature of air. It followed from Scheele's, as well as Rutherford's, observations that this new gas, which was a non-supporter of either respiration or combustion, must be one of the in-

redients of atmospheric air. The other was discovered by Scheele and Priestley.

It should be mentioned here that passages in early works suggest the possibility of a much earlier acquaintance with oxygen gas. Hoefer, in his *'Histoire de la Chimie'* (Vol. II, p. 271), claims to discover traces of a knowledge of oxygen gas in the writings of Zosimus, a Greek writer on alchemy, who lived in the third or fourth centuries. In a manuscript preserved in the National Library of Paris, entitled *'Zosimus the Panopolitan on the Sacred Art of making Gold and Silver,'* this passage occurs: "Take the soul of the copper, which is borne upon the water of mercury, and disengage an aëriform body (*'soma pneumatikon'*)." Hoefer states that here we have indications of the production of a gaseous body by means of a red substance (the soul of copper) which floats on the surface of liquid mercury; if this substance is red oxide of mercury, the "aëriform body" must have been oxygen.

Moreover, in Campbell's *'Hermippus Redivivus; or the Sage's Triumph over Old Age and the Grave,'* which was published in London in 1749, the following statement occurs: "I could mention another preparation from the vital part of the air itself, which is a great secret among these philosophers, and is perhaps the 'white dove' so often mentioned in the writings of Philalethes, of which, thus much is certain, that when the air is once despoiled of this principle, it is no longer fit for animal respiration, and it was by a contrivance of this kind that the famous Cornelius Drebbel made that liquor, which supplied the place of air in the machine he contrived for carrying on a kind of submarine navigation. This medicine, which is, as I have said, extracted from the air, is whiter than the snow, colder than ice, and so volatile that if a quantity of a nutmeg be exposed to the air it is absorbed thereby in the space of a few seconds." As Bolton has remarked, this passage refers "in an unmistakable manner to the prepara-



tion of oxygen and its property of supporting life." Drebbel (1572-1634) appears to have rowed in a boat under water in the Thames River for a distance of about eight miles, and his employment of compressed oxygen gas, if it may be so interpreted, must have been about the beginning of the seventeenth century.

Scheele prepared oxygen by heating black oxide of manganese with sulphuric or arsenic acid, and also from nitrates, and from the oxides of mercury and silver, and noted its characteristics very clearly. Priestley, who also observed the gas at about the same time, without, however, recognizing its peculiar nature, first isolated it for certain on August 1st, 1774, by heating red oxide of mercury; and as he published his results earlier than Scheele, he has generally been regarded as the first discoverer of oxygen. Both observed that this gas was capable of supporting combustion and respiration in an intensified degree. Priestley named it "dephlogisticated air," and Scheele at first 'aer vitriolicus,' later 'fire-air,' and also 'life air.'

The discovery of oxygen enabled both Scheele and Priestley to recognize air as being a mixture of two kinds of gas; Priestley calls nitrogen 'Phlogisticated air,' and Scheele terms it 'spent air.' Priestley employed salt-peter gas (nitric oxide) as an absorbent for oxygen, while Scheele made use of phosphorus, hydrate of protoxide of iron, mixtures of iron and sulphur, and moist iron filings. Both made the important observation that, upon burning a candle in an enclosed volume of air, exactly as much "fixed air" (carbon dioxide) was generated as oxygen had vanished.

Notwithstanding all this, they did not arrive at the correct explanation of combustion, respiration and calcination, whose analogy to one another they clearly saw.

The breathing of animals and the burning of substances were supposed to load the atmosphere with phlogiston. Priestley spoke of the atmosphere as being constantly "viti-ated," "rendered noxious," "depraved," or "corrupted" by

processes of respiration and combustion; he called those processes whereby the atmosphere is restored to its original condition (or "depurated," as he said), "dephlogisticating processes." As he had obtained his "dephlogisticated air" by heating the calx of mercury, Priestley was forced to suppose that the calcination of mercury in the air must be a more complex occurrence than merely the expulsion of phlogiston from the mercury; for, if the process consisted only in the expulsion of phlogiston, how could heating what remained produce exceedingly pure ordinary air? It seemed necessary to suppose that not only was phlogiston expelled from mercury during calcination, but that the mercury also imbibed some portion, and that the purest portion, of the surrounding air. Priestley did not, however, go so far as this; he was content to suppose that in some way, which he did not explain, the process of calcination resulted in the loss of phlogiston by the mercury, and the gain, by the dephlogisticated mercury, of the property of yielding exceedingly pure or dephlogisticated air when it was heated very strongly.

Consequently, the path distinctly indicated by his own observations was left for another to tread. It was Lavoisier who was destined to do this, as he easily threw aside the trivial phlogistic misconceptions that he cherished at the commencement of his scientific career. The others, indeed, supported a contradictory explanation of combustion and analogous processes, in order to remain loyal to the phlogistic doctrine. But that it was Priestley and Scheele, who, by their exhaustive investigations on oxygen and the part which it played in the processes mentioned, furnished the experimental material for the correct interpretation of these, and not Lavoisier, is beyond all question. It remained for the latter, however, to give the correct explanation of combustion, calcination and similar processes.

Among the treatises on air which appeared during this period, other than those mentioned, were Bohn's 'Medita-

tiones physico-chymicae de aëris in sublunaria inflexu' (1685); Arbuthnot's 'An Essay concerning the Effects of Air on Human Bodies' (1751); and Cavallo's 'A Treatise on the Nature and properties of Air and other permanently elastic Fluids' (1781).

In order to appreciate the advances which the chemical ideas of the Phlogistic Period showed upon those of the periods already discussed and to understand the connection which exists between the theoretical views of the phlogistonists and those of the chemists of the Modern Period, it is necessary to become acquainted with their views regarding elements, chemical compounds and chemical affinity.

Boyle's definition of an element—that it is any substance which cannot be further decomposed—was one of great significance for the whole of natural science. He also considered that the elements attainable by chemical investigation were not the ultimate constituents of matter. Nevertheless, his contemporaries and successors, failing to appreciate these views, exhibit a tendency to revert to the alchemistic elements and even to those of Aristotle. For instance, Lefevre, author of a treatise on theoretical chemistry, and Lemery classified earth and water with the three elements of Basilius Valentinus and Paracelsus, while Becher held to those three under other names—the “vitriifiable,” the “inflammable,” and the “mercurial” earths—and added water to the list.

According to Stahl's views, sulphur consists of sulphuric acid and phlogiston; and a metal, of its metallic “calx” (oxide) and phlogiston. Therefore, the phlogistonists assumed that all products of calcination and combustion (acids and oxides) were elements, in which class of substances they also classed phlogiston itself. These erroneous assumptions kept back a knowledge of the true elements, and only after it was clearly demonstrated that instead of the escape of phlogiston, the absorption of oxy-

gen must be allowed, and in place of the assimilation of phlogiston the removal of oxygen, did that extraordinary genius Lavoisier bring light into the confusion which prevailed by his brilliant ideas and observations.

A better understanding of the composition of substances was gained by analytical chemistry, which was gradually developing during this period; but altho certain constituents of compounds could be identified and distinguished from one another, yet the proportions by weight in which substances combined were not considered, and consequently the real development of the term "chemical compound" was reserved for the period of quantitative chemistry.

The chemists of the Phlogistic Period were forced to draw their conclusions concerning the composition of substances from analogy, notwithstanding which fact, however, several contributed materially to an insight into the nature of chemical compounds. Robert Boyle, for example, recognised the dissimilarity of such substances to elements, while he, Mayow, and Boerhaave stated that the characteristic properties of substances which combine chemically disappear after such combination, notwithstanding the fact that they are still present in the compound formed. Acids, salts and oxides ("calces") were, however, regarded as being of similar composition; and, until it was recognised that salts were produced by the combination of acids with bases—an achievement of this period—the term "salt" was applied promiscuously. Stahl, for instance, applied the term to acids and alkalies as well as to salts proper, and considered that salts were made up of an earth and water.

In 1745, Rouelle rendered a great service to the study of salts and the diffusion of knowledge respecting this class of compounds in his attractive lectures. He defined salts as the products of the union of acids with bases, and distinguished normal, acid and basic salts, and showed

their action on vegetable dyes. Yet he confounded many salts with acids, and could not throw off the old idea that the vitriols and other metallic salts consisted of metal and acid. Bergman demonstrated the falsity of this assumption when he proved that it is the metallic calces and not the metals themselves which combine with acids to form salts. After the time of Rouelle, solubility in water and taste were no longer regarded as characteristics of salts, inasmuch as he classed several insoluble compounds among them.

Important work on chemical affinity was contributed during this period, notwithstanding the fact that the old assumption that those bodies have an affinity for one another which have something in common—that affinity is governed by this, remained a mental fixture with speculative chemists even into the eighteenth century. The term "affinitas," used by Albertus Magnus to express this idea, presupposed the similarity of substances which interact chemically. As is generally the case, another idea evolved itself, and has lived until the present time, side by side with the first, to which it is exactly contradictory; this considers union as dependent upon contrast, on polar difference, on an effort to fill up a want. This contrary idea found a devoted exponent in Boerhaave, who maintained that it is unlike substances which show the greatest tendency to combine with each other. His influence secured the general adoption of his views by chemists.

After the time of Glauber, and particularly after that of Boyle, much attention was paid to the processes in which the forces of affinity show themselves. Cases of so-called simple elective affinity ("attractio electiva simplex," a term which originated with Bergman) were interpreted correctly by both the chemists just named, and also by Mayow; for instance, the expulsion of ammonia from salmiac by fixed alkali, by the assumption that the attraction

of the latter for hydrochloric acid was greater than that of this acid for the ammonia (fluchtiges Laugensalz). Observations of this kind on the expulsion or precipitation of bases or acids from salts, by substances endowed with stronger powers of affinity, soon caused chemists to solve the order in which analogous bodies were separated from their compounds by others. The observations on the precipitation of metals and on the expulsion of various acids from salts by means of sulphuric and nitric acids, among others, may have tended in an especial degree to make clear the different strengths of affinity in analogous bodies.

Stahl, the founder of the phlogistic theory, contributed important work on affinity. He attempted (1720) to classify the effects of affinity by arranging similar substances in a series in the order in which they expel one another from a compound: "The following mechanical experiment may serve as an example. Dissolve silver in nitric acid, it will take up the silver and appear as a light liquor; into the clear and transparent liquor throw thin strips of copper foil, the nitric acid will dissolve these and will drop the silver in the form of a powder; pour this clear green solution on to lead foil, it will be attacked and the copper previously dissolved will be dropped; pour off the clear solution and pour it on to zinc, it will dissolve the zinc and allow the previously dissolved lead to drop; into this clear solution put chalk, it will be dissolved and the zinc dropped; then to this solution add spirits of urine, which will combine with it, releasing the chalk; and finally drop in lye, the solution will take it up and allow the volatile salt to go."

Geoffroy used such a classification as the basis of his tables of affinities, 'Tables des Rapports' (1718), an arrangement destined to become very popular. The principle was to arrange similar substances so that the one following was always expelled by the one preceding from combination with the one heading the list. When thus

represented, Stahl's example just quoted becomes: Nitric Acid: potash, ammonia, lime, zinc, lead, copper, silver.

But yet another most important discovery concerning the action of affinity is due to Stahl. He recognised the fact that a reaction occurring at one temperature in one direction could be reversed at another temperature; that at ordinary temperatures calomel is decomposed by silver, while under the influence of heat silver chloride is decomposed by mercury. Such reciprocal reactions led to the suggestion to prepare tables of affinity for medium and high temperatures, both for wet and dry (*i.e.*, fusion) reactions. Bergman made the attempt in 1775 to work out this proposal of Baume's by investigating the mutual behavior of a very large number of compounds, with the result that the doctrine of chemical affinity was materially advanced, in so far as this was possible by such empirical work.

Bergman's work on affinity was published in his 'Opuscula physica et chemica.' His views may be summarized as follows: (1) There is a sequence in the magnitude of the elective affinities of a series of substances toward one with which they all combine, and this is manifested by the fact that the one possessing the greater affinity, expels from the combination the one possessing the lesser affinity. (2) This order is constant under each of the two different conditions of interaction in the moist and dry way respectively, but differs under these two distinct conditions. (3) The substance of lesser affinity is completely expelled by that of greater affinity, subject, however, to the possibility that the mass of the expelling substance may have to be very much greater than that required for simply replacing the expelled substance in the combination. (4) It is impossible to reverse such a reaction.

The following abstract from the table of Bergman on affinity will indicate the principles upon which it was based:



Sulphuric acid.	
Wet way.	Dry way.
Baryta	Phlogiston
Potash and soda	Baryta
Ammonia	Potash
Alumina	Soda
Zinc oxide	Lime
Iron oxide	Magnesia
Lead oxide	Metallic oxides
Copper oxide	Ammonia
Mercury oxide	Alumina
Silver oxide	

Potash.	
Wet way.	Dry way.
Sulphuric acid	Phosphoric acid
Nitric acid	Boracic acid
Hydrochloric acid	Arsenic acid
Phosphoric acid	Sulphuric acid
Arsenic acid	Nitric acid
Acetic acid	Hydrochloric acid
Boracic acid	Acetic acid
Sulphuric acid	
Carbonic acid	

In the table the order from top to bottom gives the relative displacing power. Thus in combination with sulphuric acid, where the action takes place in aqueous solutions, baryta is represented as displacing any of the substances placed below it, and so with potash, ammonia, etc. Where the dry substances are subjected to heat, the order is changed somewhat.

It was recognised then that the strength of affinity varied with the temperature. This is the "attractio electiva simplex" of Bergman. He recognised also an "at-

tractio electiva duplex." Macquer made use of the term "affinitas reciproca," where two bodies seemed to have nearly the same strength of affinity for a third substance, one replacing the other under slightly changed conditions—a partial recognition of the fact that affinity is dependent upon other conditions besides temperature.

This should have sufficed to show the unreliable character of the various tables offered, but chemists were slow to give them up. Nor did they value at its true worth the remarkable work of Berthollet in the next period and his conclusion that the action of affinity was proportional to the masses of the interacting substances. This, properly understood, entirely did away with all such tables, for a body with lesser affinity could displace one of greater, provided it was present in a sufficiently greater mass.

Among the chemists of this period who wrote treatises on the subject of affinity may be mentioned Limbourg (1761), Marherr (1762), Wenzel (1777), Keir (1778), Wiegleb (1780), Elliot (1786), Guyton de Morveau (1786), and Schmieder (1799).

The growth of applied chemistry during the Phlogistic Period is next to be recorded. This division of the science was especially assisted in its development by that indispensable branch, analytical chemistry, in which notable advances were made.

Qualitative chemical analysis, which had its beginnings in the iatro-chemical period, was developed by the investigations of Boyle, Hoffmann, Marggraf, Scheele and Bergman. The first named introduced the word "analysis" for those chemical reactions by which individual substances could be detected in the presence of one another, and considerably advanced the analytical examination of substances in the wet way. He employed reagents to distinguish the important classes of compounds, and the systematic use of plant juices as indicators for the detection of acids, bases and neutral substances originated with him. For this purpose, he used the coloring matters in the juices

of litmus, violets and corn-flowers. Among the other reagents he introduced may be mentioned solutions of calcium and silver salts for the recognition of sulphuric and hydrochloric acids respectively, infusions of oak leaves or gall nuts for the detection of solutions of the salts of iron, and volatile alkaline salt for the recognition of copper salts. He recognised ammonia by the white cloud that resulted when it came in contact with fuming acids, such as hydrochloric or nitric acids.

Hoffmann busied himself in analytical chemistry mainly with the investigation of mineral waters. He examined many samples, and showed that they contained carbonic acid, iron, common salt and salts of magnesia and lime. He furnished valuable information as to the methods of testing for these substances, and also indicated many characteristics of mineral waters. The 'Tabelle über einige 40 Mineralwässer' was an important contribution by Carl A. Hofmann (1789).

Marggraf, besides proving that gypsum consisted of lime and sulphuric acid, and that the latter was also a constituent of heavy spar, made use of the different colorations which the salts of soda and potash impart to a flame as a means for their recognition, and employed a solution of prussiate of potash as a test for iron.

Scheele made many valuable observations in analytical chemistry. He it was who perceived the difference between soluble and insoluble silicic acid, and effected the separation of iron and manganese by acetic acid, in addition to independently observing the flame colorations of salts of soda and potash, and explaining the difference between the inner and outer flames of the blowpipe, a piece of apparatus which was introduced into chemistry by Gahn, Cronstedt and Bergman. The latter was indebted to Scheele for many observations, but was more systematic than his contemporary. He suggested the use of sublimate, liver of sulphur, and sugar of lead as reagents; of hydrochloric acid or carbonate of potash to open up ores;

and of methods for the separation of salts and the estimation of precipitates. The tests he employed for the recognition of sulphuric, hydrosulphuric, carbonic, arsenious and oxalic acids, and of lime, baryta and copper, are still in use.

Bergman was, to quote von Meyer, "probably the first to proceed on the principle that an element should not be itself isolated and estimated according to its own weight, but separated in the most convenient form as an insoluble precipitate—*e.g.*, lime earth as oxalate of lime, and sulphuric acid as sulphate of baryta," in the determination of the weights of metallic precipitates. This procedure, in conjunction with the endeavors of Marggraf, Homberg, Scheele and Black, to take the proportions by weight into account—in other words, to determine the quantity of a substance or substances present in a solution—furnished important preparatory work for the quantitative investigations of the next period.

In the analysis of gases, the most noteworthy work of the period was done by Cavendish, who made a determination of the amount of oxygen in the air by exploding with hydrogen. He found that the oxygen amounted on the average to 20.85 per cent., a result which is only 0.05 per cent. short of the mean as determined at the present day. It was learned that carbonic acid and oxygen could be estimated volumetrically by the use of absorptives: caustic potash was used for the absorption of the former, and phosphorus for that of oxygen.

Mainly owing to the efforts of such investigators as Boyle, Kunckel, Marggraf and Duhamel du Monceau, technical chemistry made considerable progress during the Phlogistic Period.

In metallurgy, correct explanations of many processes were brought out, altho in general it may be said that the methods of extracting metals from their ores underwent little improvement. In the manufacture of iron and steel, however, some material changes were made as a result of

the investigations of Bergman, Gahn, Rinman and Rene Reaumur. The latter's work, "*L'Art de convertir le fer forge en acier et l'art d'adoucir le fer fondu, ou de faire des ouvrages de fer fondu aussi fin que de fer forge*," published in Paris in 1722, brought the author a pension of 12,000 francs from the Duke of Orleans, because of the improvements it effected in the manufacture of cast iron and steel. An account of Reaumur's method of softening cast iron was also embodied in Horne's '*Essays Concerning Iron and Steel*,' a work of useful observations published in London in 1773. Duhamel improved the manufacture of brass, and Marggraf introduced a more satisfactory method of preparing zinc from calamine.

A valuable treatise by Kunckel on the ceramic art and glass-making appeared in 1689. This work was entitled '*Ars vitraria experimentalis*,' and contained Neri's '*Arte vitraria*,' with additions by Kunckel and others. After the introduction of the importation of chinaware, many attempts were made to imitate this true porcelain. In this, Böttger (1685-1719) made the first advance in 1709, altho it is now known that a porcelain of soft paste was made at Florence as early as 1580. Böttger first made a red ware, but eventually, by employing kaolin, he made a true porcelain at Meissen. The process of manufacture remained a secret, however, and it was not until it was solved at Sevres in 1769 by the experimental work of Reaumur and other chemists that the manufacture spread.

In England, porcelain appears to have been experimentally manufactured at Fulham, by Dwight, as early as 1671; but it was not produced in quantity until about 1730, when works were established at Bow. In this connection, Higgins' '*Experiments and Observations made with the view of Improving the Art of composing and applying Calcareous Cements*' (1780) should be mentioned. This treatise contained the results of valuable experimental investigations on the induration and strength of cements.

Two works of great aid to the dyer—Macquer's '*L'Art de*

la teinture en soie' (1763), and Hellot's 'L'Art de la teinture des laines et etoffes de laine' (1750, 1786)—in that they contained speculations upon the manner in which dyeing operations are carried out, appeared during this period. Stahl, Hellot and Macquer divided dyes into two classes, viz., those capable of being fixed on cloth without the aid of mordants, and those requiring the use of such agents, and in 1794, Bancroft distinguished these divisions as adjective and substantive dyes. Prussian blue was discovered by Diesbach in 1710.

Sulphuric acid, the manufacture of which constitutes one of the most important branches of modern technical chemistry owing to the great variety of purposes for which it is required, was first manufactured on a large scale by a quack physician of the name of Ward, about the middle of the eighteenth century. For this manufacture, he employed glass globes of about 40 to 50 gallons capacity; a small amount of water having been poured into the globe, a stoneware pot was introduced, and on this a red-hot iron ladle was placed. A mixture of sulphur and saltpeter was then thrown into this ladle, and the vessel was closed. The vapors evolved were absorbed by the water, and sulphuric acid costing from 1s. 6d. to 2s. 6d. per pound was obtained. Roebuck of Birmingham was the first to suggest the use of leaden chambers instead of glass globes. These leaden chambers were set up in Birmingham in 1746, and were worked intermittently; the continuous working of them is an achievement of the nineteenth century.

The manufacture of fuming sulphuric acid was first carried out at Nordhausen in the Harz, by heating roasted green vitriol, but was subsequently removed to Bohemia. Rouelle demonstrated that nitric acid could be concentrated by distillation with sulphuric acid. A number of improvements were made in the manufacture of this acid by Stahl and other chemists, but hydrochloric acid was not prepared in large quantities, as it was not employed

technically. As early as 1670, an artist, Henry Schwanhard, prepared hydrofluoric acid for etching figures on glass, and it is probable that his preparation was the same as that known to some artists as a secret in 1721, and published by Weygand in 1725.

The alkalis and their carbonates were obtained just as in ancient times, viz., from the ashes of plants, incrustations on the soil, and carbonized tartar. However, it was shown by Duhamel and other chemists that common salt could be converted first into sulphate of soda, and finally into carbonate of soda. A description of such a process is contained in the 'Description de Divers Procèdes pour Extraire la Soude du Sel Marin,' published by the 'Imprimerie du Comite de Salut public' in 1795. Duhamel also introduced suitable methods of preparing starch and soap, and improved the processes of manufacturing sal ammoniac and sugar. His 'L'Art de raffiner le sucre' (1764) was held in high esteem in this period. Marggraf's discovery of cane sugar in the juice of the red beet has been referred to; it only remains to say that it laid the foundation for the now enormous and important beet sugar industry.

The knowledge of the chemical elements and compounds was enlarged to a remarkable degree in the Phlogistic Period, and the discoveries made and facts learned afterward became of great technical importance. Six new elements—chlorine, phosphorus, manganese, cobalt, nickel and platinum—were added to the ones already known. Phosphorus was obtained by Brand, a Hamburg alchemist, in 1669, by distilling the residue from evaporated urine; he called it "cold fire," and in 1671 Johann Elsholtz, of Vienna, gave it the same name as the Bologna stone, or "phosphor," which was discovered about 1603. The discovery of phosphorus caused much excitement on account of its properties, but its preparation was kept secret, and it was only after many endeavors that Boyle and Kunckel



discovered the method of obtaining it. The "phosphorus" described by Balduinus in 1675 is thought to have been dry calcium nitrate, while that discovered by Homberg in 1693 was an oxychloride of calcium. Kunkel, in several treatises on phosphorus, gave an account of its discovery and contributed to a better knowledge of the element.

The first account of metallic manganese was given in the 'De metallis dubiis' of Jacob Winterl and J. G. Kaim, which was published in Vienna in 1770. Gahn, however, is generally credited with its isolation, which he effected in 1774. Cobalt was discovered by Brandt in 1742, and the earliest full account of the metal is contained in Johann Gesner's 'Historia cadmiæ fossilis metallicæ sive cobalti,' which appeared the next year. Nickel was first prepared by Cronstedt in 1750. The observations of Arvidson on this interesting metal were published in 1775.

Platinum is first referred to in Don Antonio de Ulloa's 'Relacion historica del viaje a la America Meridional' (1748). William Watson, an English chemist, was the first to examine the "Platina di Pinto," found in the Spanish West Indies by explorers, and his observations, along with Brownrigg's experiments on the metal, were published in the 'Philosophical Transactions' of the London Royal Society in 1751. Watson's experiments were continued by Lewis in 1755, Macquer in 1758, and Marggraf in 1761. De Buffon asserted that platinum was an alloy of gold and iron, and von Milly considered that it contained these metals, together with mercury. Its elementary nature was not established to the satisfaction of all until the next period.

The knowledge of organic compounds was also considerably extended, and new fields for organic chemistry were opened up toward the close of the period. However, the real composition of all organic compounds was not ascertained until the time of Lavoisier.

Boyle investigated dry distillation, and proved that the

liquid obtained by the distillation of wood is not a simple body, but that it contains, besides pyroligneous acid, an indifferent body which may be separated by distillation over burnt coral. The crude wood-spirit thereby procured he termed "adiaphorous spirit." He also wrote on the production and rectification of alcohol, a subject of frequent investigation by the chemists who followed him. Spirit of wine was prepared fairly pure, and was used in analytical chemistry for the separation of various salts, but confused opinions were held with respect to its formation in spirituous fermentation processes.

Attempts were made by Reaumur in 1733, and Mathurin Brisson in 1768, to determine the amount of alcohol in aqueous solutions containing it from its specific gravity. An interesting treatise on wines, 'Ueber die Verfälschung der Weine,' was written by Friedrich Cartheuser in 1779. Frobenius (1730), Hoffmann, Pott, Antoine Baume (1757), and Cadet de Gassicourt (1775) investigated ether ("spiritus vini vitriolatus"), but until 1800 it was believed to contain sulphur. A mixture of ether with alcohol, known as "Hoffmann's drops," and the compound ethers were used officinally.

Scheele discovered, or first clearly distinguished, the important organic acids, showing that grapes contained one (tartaric acid) which differs from that found in lemons (citric acid); that another (malic acid) occurred in apples, and again a new one (oxalic acid) was detected in wood-sorrel. The latter he prepared by the oxidation of cane-sugar with nitric acid, and found that it differed from the one obtained by treating milk sugar with nitric acid (mucic acid). He also discovered lactic acid in sour milk, uric acid in bladder stones, and prussic acid by decomposing yellow prussiate of potash with sulphuric acid; and improved the methods of preparing gallic and benzoic acids. He showed that the latter forms a lime salt freely soluble in cold water, and therefore may be readily obtained by boiling gum benzoin with milk of lime, con-

centrating the filtrate and separating the acid by means of hydrochloric acid. On the other hand, he learned that malic, tartaric and citric acids formed insoluble salts with lime or lead oxide, by the aid of which substances they might be separated from other bodies in the fruit. He prepared the acids by decomposing their lime or lead salts thus obtained with sulphuric acid.

Formic acid was discovered by Wray in 1760, and was further investigated by Arfvidson and Cehrén in 1777. Its resemblance to acetic acid, which was now prepared in a pure form, was soon observed, and this produced some confusion. Marggraf proved that they differed.

Oils and fats were frequently investigated, and Scheele showed that they contained a common constituent, oelsüss, or the "sweet principle of oils." This is now known as glycerin, or glycerol. Scheele stated that it is related to sugar, not only because of its taste, but also on account of the fact that both substances yield oxalic acid in treatment with nitric acid. The importance of this discovery was not realized until a much later date.

Considerable progress was made during this period in medical and pharmaceutical chemistry, and many new medicines came into vogue. Among these were carbonate of ammonia, sulphate of potash, magnesia alba and sulphate of magnesia.

Among the text-books which appeared may be mentioned the following: the 'Manuductio ad chemiam pharmaceuticam' of Rivinus (1690); Fick's 'Chymicorum in pharmacopœia Bateana et Londinensi explicatio' (1711); von Ludolff's 'Die in der Medicin siegende Chemie' (1750), and Baume's 'Elements de Pharmacie Theorique et Pratique' (1762). The advances made in organic and medical chemistry prepared the ground for physiological chemistry, a branch which has been greatly developed in the most recent period.

## CHAPTER IX

### LAVOISIER AND THE ANTIPHLOGISTIC CHEMISTRY

It has been seen how far the development of chemical knowledge during the seventeenth century was influenced by Stahl's phlogistic theory—that this theory exerted a decided influence on the progress of chemistry, but that it was too elastic to give exact definition to the tendency of investigation. It had, however, done good work, since it coördinated facts and developed unity of purpose, and served admirably as a period of preparation for the scientific experimental work of the era commencing with the discovery of oxygen by Scheele and Priestley—the Modern Chemical Period. For twenty years following this discovery a contest concerned mainly with the recognition of the experimental method was pursued. It had to do with the support of the method of observation under definite conditions as the foundation of all theoretic inferences and views, and with the subduction of the prejudices which had resulted from following the method which fostered speculation and the adaptation of observations, as far as possible, to the established system.

This short period of revolution (1774-1794) is rendered radiant by the reforms of one of the most remarkable men in the history of science, Lavoisier, who abolished old prejudices and masterfully applied scientific principles to the explanation of chemical phenomena. His combustion theory supplanted the doctrine of phlogiston—a change, it is true, that primarily only required the substitution of

the words "addition of oxygen" for "withdrawal of phlogiston," but which eventually resulted in a complete transformation of all ideas concerning combustion, calcination and respiration, and consequently the views respecting chemical composition—a displacement which culminated in the conversion of the chemistry dominated by the dogma of Stahl into the antiphlogistic system, the "New Chemistry."

The Phlogistic Theory was deposed by the Theory of Oxygen, but, as Whewell has pointed out, "this circumstance must not lead us to overlook the really sound and permanent part of the opinions which the founders of the phlogistic theory taught." In this connection, we must not forget how much Lavoisier owed to his predecessors. He sifted and collated the facts handed down to him by the phlogistonists, and, mainly from the standpoint of the physicist, gave correct explanations of many processes; but he made no independent chemical discoveries, and is honored not as a Scheele or Black, but as the founder of a new system based on his comprehensive and correct explanations of the observations of other investigators. Consequently, it may be said that Gallic patriotic bias prompted Wurtz to state in his "*Histoire des Doctrines Chimiques*" that "*La chimie est une science française*"—an assertion which was repeated twenty years later by Jagnaux. Since, however, chemistry only took rank as a science when quantitative work was made its basis, Lavoisier must be given credit above all others in having directed it into and along this road.

Antoine Laurent Lavoisier was born in Paris on the 26th of August, 1743. His father was wealthy and spared no expense on his education. In his twenty-first year Lavoisier obtained a gold medal from the Academy of Sciences for an essay on the most appropriate method of lighting the streets of Paris, but it was some years before he made definite choice of his subject. He published memoirs relating to geology and to mathematics, before the

fame of Black's and Priestley's discoveries reached him and induced him to turn his attention to scientific chemistry.

By good business management he greatly added to his property and became a man of wealth. He lived well, giving dinners which were famed for their excellence and for the company gathered at them. This attracted attention to him and won for him some enemies whose influence was felt in the storm gathering against all that smacked of aristocracy. In addition, he was a *fermier-général*; and tho he brought about some reforms, some of his measures proposed to the Government were exceedingly unpopular, as, for instance, his plan for taxing Paris. Impeached under the Reign of Terror, he was condemned to death, and was executed, together with twenty-eight other *fermiers-généraux*, on the 8th of May, 1794.

In Lavoisier is seen a master mind, not only capable of devising and conducting experiments, but mainly of assimilating those of others, and deducing from them their correct significance. Altho his additions to the known chemical compounds were few in number, and cannot, as mentioned, be compared with those of Scheele or of Priestley, yet his reasoning in disproof of the phlogistic theory was so exact that it rapidly secured conviction, and laid the foundation for the new chemistry of the quantitative era. Hitherto exclusive importance had been attached to visible phenomena, but Lavoisier introduced a more exhaustive investigation of chemical reactions and the relations of quantity. The important work in which he recognised and explained the part played by oxygen in the process of combustion, calcination, and respiration embodies the chief investigations of his life, however, and in this lies his abiding service to science.

The earlier observations of Rey, Mayow, and others, who had attributed the increase in weight of the metals during their calcination to an absorption of air, contained only the first germs of the true explanation of these proc-

esses. From the year 1772 Lavoisier engaged in investigations bearing upon this subject, the first results of which he delivered in a sealed note to the French Academy on November 1st of that year. This note was to the following effect:

"About eight days ago I discovered that sulphur, when burned, instead of losing weight, gains weight; that is to say, from one pound of sulphur much more than one pound of vitriolic acid is produced, not counting the moisture gained from the air. Phosphorus presents the same phenomenon. This increase of weight is due to a great quantity of air which becomes fixed during the combustion, and which combines with the vapors. This discovery, which I confirmed by experiments which I regard as decisive, led me to think that what is observed in the combustion of sulphur and phosphorus might likewise take place with respect to all the bodies which augment in weight by combustion and calcination; and I was persuaded that the gain of weight in calces of metals proceeded from the same cause. Experiment fully confirmed my conjectures. I effected the reduction of litharge in closed vessels with Hales' apparatus, and I observed that at the moment of the passage of the calx into the metallic state, there was a disengagement of air in considerable quantity, and that this air formed a volume at least a thousand times greater than that of the litharge employed. As this discovery appears to me to be one of the most interesting which has been made since the time of Stahl, I thought it expedient to secure to myself the property, by depositing the present note in the hands of the secretary of the Academy, to remain secret till the period when I shall publish my experiments. LAVOISIER."

He was, however, in the same position as Mayow had been—that is, still in doubt as to which portion of the air caused this increase in weight, as to the air itself being a mixture of gases, and especially as to the nature of the



process which occurred in the reduction of the litharge; he felt inclined to regard the generated gas (carbonic acid) as the fluid originally combined with the lead. This uncertainty was brought about by his giving little attention to the qualitative side of the chemical reactions.

In 1774, after repeating these and similar investigations, Lavoisier found his error with regard to the reduction of litharge, and furnished more elaborate details of his observations, especially of the calcination of tin. He began by considering the possible solutions of the problem, and then investigated what changes really do occur, from which he inferred the cause. To quote from his "Œuvres":

"Thus then did I at the beginning reason with myself: if the increase in the weight of metals calcined in closed vessels is due, as Boyle had thought, to the addition of the matter of the flame and the fire which penetrate the pores of the glass and combine with the metals, then it follows that on introducing a known weight of metal into a glass vessel and sealing this hermetically, determining the weight exactly, and then proceeding to calcination by a charcoal fire—just as Boyle had done—and then finally after calcination, before opening it, again weighing the same vessel, this weight must be found augmented by that of the whole quantity of fire matter which had been introduced during calcination. But if, said I to myself, the increase in the weight of the metal calx is not due to the addition of fire matter nor of any other extraneous matter, but to the fixation of a portion of the air contained in the vessel, the whole vessel after calcination must be no heavier than before and must merely be partially void of air, and the increase in the weight of the vessel will not occur until after the air required has entered."

To test these theoretical considerations, Lavoisier selected the calcination of lead and of tin in sealed retorts. From two careful experiments with eight ounces of tin—similar ones with lead were unsuccessful—Lavoisier found that the increase in weight of the tin on calcination was

practically identical with the weight of air which took the place of that absorbed during calcination. His conclusions were as follows:

"Summing up the results of the two experiments on tin just described, it seems to me impossible not to draw the following conclusions:

"First. In a given volume of air only a fixed quantity of tin can be calcined.

"Secondly. This quantity is greater in a large retort than in a small one.

"Thirdly. The hermetically sealed retorts, weighed before and after the calcination of the tin contained in them, showed no difference of weight, which evidently proves that the increase in weight of the metals arises neither from the fire matter nor from any other matter extraneous to the vessel.

"Fourthly. In all calcinations of the tin the increase in weight of the metal is sufficiently nearly equal to the weight of the air absorbed, to prove that the portion of the air which combines with the metal during calcination is of specific gravity approximately equal to that of atmospheric air."

Thus the problem he had undertaken had been solved by Lavoisier. He had ascertained the cause of the increase in the weight of metals on calcination and had found it to be combination with a certain portion of the air. And having proved before that sulphur and phosphorus on burning also increase in weight and absorb a large volume of air, Lavoisier must at that stage, as Freund remarks, be supposed to have established that combustion consists in combination with a portion of the atmospheric air, whereby the increase in weight on combustion is accounted for. However, he knew nothing as yet concerning the nature of the portion of air absorbed. In the time between the memoir on the calcination of tin and his next contribution to the subject of combustion, falls Priestley's discovery of a gas obtainable by the heating of red oxide

of mercury, the investigation of the properties of this gas, and the recognition that it is a better supporter of combustion than ordinary air; Lavoisier learned of this new fact, and his next paper bears evidence of the manner in which he was helped thereby.

This paper, which was written in 1775, was entitled "On the Nature of the Principle which combines with Metals during their Calcination, and which increases their Weight." In this he described experiments showing that when metallic "calces" are converted into metals by heat-

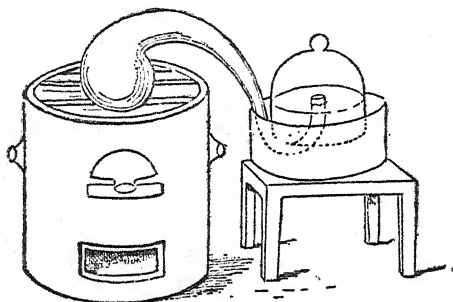


Fig. 18 —LAVOISIER'S APPARATUS FOR THE CALCINATION OF MERCURY.

ing with charcoal, a quantity of fixed air is expelled; and here for the first time he pointed out that "fixed air" is a compound of carbon with the elastic fluid contained in the 'calx.'" He then described the preparation of oxygen by Priestley's process of heating red oxide of mercury ("mercurius precipitatus per se"), and showed that the red oxide, when heated with charcoal, exhibited the properties of a true "calx," inasmuch as metallic mercury was formed and a large quantity of "fixed air" was produced.

In 1776, Lavoisier observed that the combustion product of the diamond was composed of carbonic acid alone; and in his next paper, which appeared the following year, he

dealt with the combustion of phosphorus; he recapitulated Rutherford's experiments, and showed that one-fifth of the air disappeared, and that the residue, to which he gave the name "mouffette atmosphérique," is incapable of supporting combustion. As mentioned, Rutherford named this residue "phlogisticated air," since he imagined it to have absorbed phlogiston from the burning phosphorus; Scheele, too, had made a similar experiment with a like result. From these observations, Lavoisier concluded that air consists of a mixture or compound of two gases, one capable of absorption by burning bodies, the other incapable of supporting combustion.

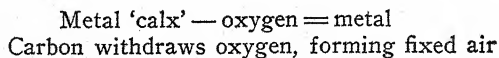
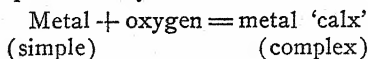
The results of these investigations, along with the observations of Scheele and Priestley, and a research on the combustion of organic substances made in 1777, the products of which he showed to be water and carbonic acid, enabled Lavoisier to enunciate his views on combustion in a memoir published in 1778. The main points of this combustion or oxidation theory are as follows:

(1) Substances burn only in pure air ('air éminement pur').

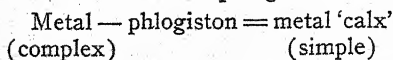
(2) This air is consumed in the combustion, and the increase in weight of the substance burnt is equivalent to the decrease in weight of the air.

(3) The combustible body is, as a rule, converted into an acid by its combination with the pure air, but the metals, on the other hand, into metallic 'calces.'

Hence the mechanism of combustion according to Lavoisier is represented by:



in direct contradiction to the phlogistic scheme:



In 1783, there appeared a memoir by Lavoisier, entitled "Reflections concerning Phlogiston." After explaining the phenomena of combustion and reduction as combination with oxygen or its separation, he proclaimed the non-existence of phlogiston, saying in part as follows:

"But if in chemistry everything can be satisfactorily explained without the aid of phlogiston, it thereby becomes eminently probable that such a principle does not exist, that it is a hypothetical being, a gratuitous assumption, and sound logic is opposed to unnecessary complication. Perhaps I might have confined myself to these negative proofs and remained content to show that the phenomena can be better explained without phlogiston than by means of it; but the time has come when I must speak out in a more definite and formal manner concerning a view which I consider an error fatal to chemistry, and which appears to me to have considerably retarded progress by the method of false reasoning it has engendered. All these reflections prove what I have advanced, what it has been my object to demonstrate, what I will repeat once more, namely, that chemists have turned phlogiston into a vague principle, one not rigorously defined, and which consequently adapts itself to all the explanations for which it may be required. Sometimes this principle has weight and sometimes it has not; sometimes it is free fire and sometimes it is fire combined with the earthly element; sometimes it passes through the pores of vessels, sometimes these are impervious to it; it explains both causticity and non-causticity, transparency and opacity, colors and their absence; it is a veritable Proteus, changing in form at each instant."

It was in this year that his important memoir upon the composition of water appeared, and it was this research which removed the last obstacles with which the antiphlogistic system had to contend.

James Watt, the Scotch inventor, was the first to state distinctly that water is not an element, but that it is com-

posed, weight for weight, of two other substances, one of which he considered to be phlogiston and the other "dephlogisticated air"; and John Waltham, a friend of Priestley, was one of the first chemists to note the deposit of moisture on the inside of a tube after exploding a mixture of air and "inflammable gas." To Cavendish, however, belongs the credit of having first supplied the correct experimental basis upon which accurate knowledge

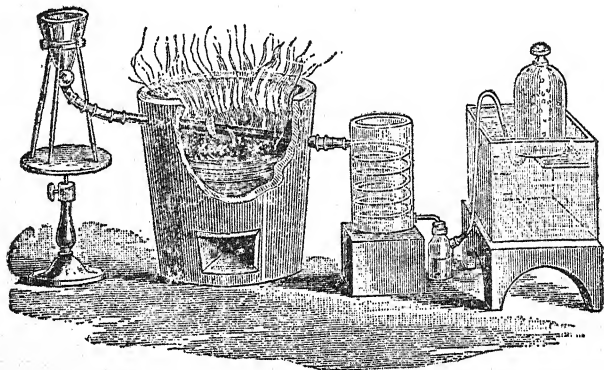


Fig. 19 —LAVOISIER'S APPARATUS FOR THE ANALYSIS OF WATER.

could alone be founded. When Lavoisier learned that Cavendish had proved that water alone is produced by the combustion of hydrogen—information which was imparted to him by Sir Charles Blagden in 1782—he immediately repeated Cavendish's experiments on a large scale, and was assisted on that occasion by Laplace, Blagden also being present. A large quantity of water was produced, and the volumes of the combining gases were found to be 1 of oxygen to 1.91 of hydrogen. Not long after, in conjunction with Meunier, he performed the converse operation, in decomposing steam by conducting it over iron wire heated to redness in a porcelain tube. The iron removed

the oxygen from the water, while the hydrogen passed on and was collected in the gas-holder.

The explanation of the solution of metals in acids was now simple: it depended on the decomposition of water. While the oxygen combined with the metal to form a 'calx,' the hydrogen was evolved; the 'calx' dissolved in the acid, forming a salt of the metal. The operation of producing hydrogen by the action of steam on red-hot iron met with an equally easy explanation: the oxygen and iron united to form an oxide—the ancient "ethiops martial"—while the hydrogen escaped. The converse occurred during the reduction of a 'calx' to the metallic state by hydrogen. In this case the hydrogen seized on the oxygen of the 'calx,' removed it in the form of water, and the metal was left. These experiments were due to Cavendish; all that Lavoisier did was to indicate and prove the true nature of the phenomena. The opponents of the new doctrines, Priestley prime among them, exerted themselves to disprove the view that water was a compound of oxygen and hydrogen. But their efforts were in vain. Many of Lavoisier's opponents had to admit the justice of his views; and chemists of standing commenced the application of his ideas, first in France (Berthollet 1786, de Morveau, and the cautious Fourcroy not until 1787), and soon in other countries also (Kirwan, *e.g.*, in 1792). Lavoisier's critical treatises, which were directed to showing the untenability of the phlogistic theory, conjoined with his "Traité de Chimie," gave the final blow to that doctrine. The new doctrine was accepted by the most prominent chemists after the comparatively short time which was required to put it to the proof. From the year 1792, after Klaproth, following Hermbstädt, Girtanner, etc., in Germany, Kirwan and Higgins in England, Troostwyk, Deiman and van Marum in Holland, and Giobert, Brugnatelli, etc., in Italy, had signified their adhesion to it, one may speak of the final victory of Lavoisier's system; and this, notwithstanding the fact that still many



chemists of great eminence refused to accept it in its full extent—for example, de la Métherie, Sage, and Baumé in France; Westrumb, Gren, Crell, and Wiegleb in Germany; Gadolin and Retzius in Sweden; and Cavendish and Priestley in England.

Some opponents of the new system, mainly owing to their misinterpretation of the Lavoisierian views, continued to combat it till about 1800.

As late as 1796, Lamarck, for example, wrote an attack on the Lavoisierian theory of combustion, in which he referred to the "pretended existence of a material called oxygen which the pneumatic chemists have never seen nor studied, and the existence of which they imagine to explain the effects of 'fixed acidific air.'"

A few words should be said in this connection with regard to Lavoisier's views on the relation of plants and animals to the atmosphere.

Priestley already knew that oxygen was necessary for respiration, but his unfamiliarity with accurate analytical work and his close adherence to the phlogiston theory prevented him from arriving at a true explanation of the facts he observed. Lavoisier showed how oxygen was used up in the lungs, in the formation of carbonic acid and of water, and how this process, which he properly classed as one of combustion, furnishes to man the heat necessary for his existence. He demonstrated that the expired carbonic acid derives its carbon from the blood itself; that in the process of respiration we thus, to a certain extent, burn ourselves, and would consume ourselves if we did not replace, by means of our food, that which we have burned.

The experiments which Lavoisier made on respiration show the clearness of his methods.

One of Lavoisier's earlier memoirs, that presented to the Académie des Sciences in 1770, entitled "On the Nature of Water and on the Experiments adduced in Proof of the Possibility of its Change into Earth," illustrates his

accuracy, thoroughness and acute reasoning. He states that the purpose of the research was as follows:

"I find myself confronted with the task of settling by decisive experiments a question of interest in physics, namely, whether water can be changed into earth, as was thought by the old philosophers, and still is thought by some chemists of the day."

It had been noted by many earlier investigators, that when water was boiled for a long time in a glass vessel, a mass of white residue was found in the vessel after evaporation. This was long regarded as a conclusive proof that water could be changed into earth. Lavoisier weighed his glass vessel, and then, after heating water therein for one hundred days, found there was no change in the weight of the vessel and its contents. When he evaporated the water, he obtained a residue of earthy matter which he found corresponded, within the range of experimental error, with the loss in weight of the empty vessel. He therefore concluded from his experiments, "that the greater part, possibly the whole, of the earth separated from rain water by evaporation, is due to the solution of the vessels in which it has been collected and evaporated."

Scheele afterward showed that this 'earth,' or residue, possessed the same composition as the glass, thereby confirming Lavoisier's work. The old alchemical idea of transmutation was thus shown to be false, and was finally dismissed from chemistry.

Lavoisier established the important generalization that matter may be changed, but not destroyed nor created. The matter lost from the glass vessel was merely dissolved in the water. This is the principle of the Indestructibility of Matter, the fundamental principle of modern science. However, it must be realized that while from the commencement of his experimental life Lavoisier was guided in all his reasoning by the recognition of the principle of the conservation of mass, yet it was only after he had

found this view proved by his work on combustion that he enunciated it (1785). To quote from his "Œuvres":

"Nothing is created, either in the operations of art or in those of nature, and it may be considered as a general principle that in every operation there exists an equal quantity of matter before and after the operation; that the quality and the quantity of the constituents is the same, and that what happens is only changes, modifications. It is on this principle that is founded all the art of performing chemical experiments; in all such must be assumed a true equality or equation between the constituents of the substances examined, and those resulting from their analysis."

The establishment of the law of the conservation of mass has followed curious lines. As Freund observes, Lavoisier did not arrive at it strictly inductively, by generalization from a large number of cases in which the weights of the substances participating in a chemical reaction were compared with the weights of those resulting from it. The available data of chemical investigations did not supply him with the material for so doing. The belief growing among physicists of the imponderable nature of heat, together with the old view of the indestructibility of matter in general, must have supplied him with the basis for an assumption, from which he drew deductions that were verified by the result of experiment. Generally speaking, ever since his time, the scientific world has been content to regard the conservation of mass as an axiom.

A number of Lavoisier's statements indicate that his views upon the nature of his "matière de chaleur" (matter of heat) approximate to the Mechanical Theory of heat. Thus he states that "Heat is the energy which results from the imperceptible movements of the molecules of a substance; it is the sum of the products of the mass of each molecule into the square of its velocity."

According to him, matter consists of small particles which do not touch one another, since, otherwise, a dim-

inution of volume by lowering of temperature could not be explained: the matter of heat exists between these particles. The hotter a substance is the more of the matter of heat does it contain. In the investigations into the specific heats of various substances, carried out along with Laplace, Lavoisier further proved that, for a like increase in temperature, substances do not take up like quantities of the matter of heat. Lavoisier knew that, by the addition of heat, ice is first converted into water, and the water then into steam. Hence, gases contain most of the matter of heat. This is what we should understand when he says that his 'air pur' consists of the acidifying principle and the matter of heat. During combustion the former unites with the combustible substance, and the matter of heat is liberated. It produces light and heat. Lavoisier also termed the matter of heat "calorique."

Lavoisier's views with respect to the heat liberated during combustion, altho not quite accurate, are also of great importance. He considered that when a solid substance (phosphorus) burned in gas (oxygen), and the product of the combustion was solid (phosphoric anhydride), the disengagement of heat was due to the condensation which the gas had undergone, in order that it may become solid. If the product was gaseous (carbonic anhydride), he attributed the disengagement of heat to the alteration of the specific heat. He advanced the general view that the heat of combustion must be greatest when two gases unite to form a solid substance. How correctly he understood the application of these fundamental ideas is shown by his mode of explaining the lowering of temperature produced by dissolving salts in water. Lavoisier assumed, as we do, that it is the change of state of aggregation which occasions the absorption of heat. He showed, further, that the evolution of heat which occurs on mixing sulphuric acid with water is accompanied by a decrease in volume, and that both maxima coincide; so that theory and experiment agree.

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It may be said, therefore, that Lavoisier laid the foundation for the modern thermo-chemistry.

Lavoisier also occupied himself with organic chemistry, or the chemistry of life-products, and made a beginning toward a scientific study of it by devising a method of analysis by which these bodies could be burned, and the water and carbon dioxide which were formed measured.

He heated a known weight of the substance with a known weight of red mercury oxide, and weighed the carbonic acid and water produced. He knew the oxygen content of the mercuric oxide, and so could ascertain how far this supplied the carbon and hydrogen with the oxygen they required, and how far this was furnished by the compound under investigation. Lavoisier in this way determined the composition of alcohol.

However, the whole system of quantitative organic chemistry was too young for Lavoisier to anticipate the nicety with which Liebig, later, could handle these methods of ultimate analysis; he considered his experiments to be merely confirmatory of his system, the composition of sugar a mere incident. Organic bodies in general he regarded as oxides of a radical, which might itself contain hydrogen and carbon, or in some cases these together with nitrogen, sulphur, and phosphorus.

Lavoisier adhered to Boyle's definition of an element. With him, an element was any substance which could not be further decomposed. The metals and the most important non-metals were ranked among the elements; and compound bodies like the alkalies, ammonia and the earths were numbered among these also, but not without considerable uncertainty being expressed as to their elementary nature. Oxygen, also recognised as an element, became, because of its part in combustion and its capacity for combining with so many other elements, the center point of the antiphlogistic system, which indeed owed its inception to the knowledge of the behavior of other elements toward oxygen. The importance which Lavoisier attached



to this gas is clearly shown in his theory of acids, in which he explained the properties of acids by the hypothesis of the acidifying principle being oxygen, the name of which ( $\delta\acute{\epsilon}\tau\upsilon\varsigma\gamma\epsilon\nu\rho\acute{\alpha}\omega$ , I generate acid) still bears witness to this view; and in the statement that the bases which combine with acids also contain oxygen. The composition of a large number of compounds—oxides, acids and salts—was thus rightly interpreted, the phlogistic hypothesis having regarded as simple the substances belonging to the first two of these classes.

The views of Lavoisier and his disciples with respect to elements and compounds are to be found in the treatise entitled "*Methode de nomenclature chimique*," which was published by Lavoisier conjointly with Guyton de Morveau, Berthollet, and Fourcroy, in 1787. This work, in conjunction with the "*Traité Élémentaire de Chimie*" (1789), changed the existing language of chemistry and shaped the course of progress still pursued.

In the first-mentioned treatise all substances are divided into elements and compounds. To the former belonged—in addition to light and heat—oxygen, hydrogen and nitrogen; these formed the first class. The second group contained the acid-forming elements, sulphur, phosphorus and carbon, to which were added the hypothetical radicals of hydrochloric, hydrofluoric and boracic acids. The third class comprised the metals, the fourth the earths, and the fifth the alkalies; but Lavoisier considered the elementary nature of the last of these as so improbable that in the "*Traité Élémentaire de Chimie*" he no longer included them among the elements. For the nomenclature of the latter, the old names of the metals and of some of the non-metals (*e.g.*, soufre, phosphore, etc.) were retained, while Lavoisier's new names for others of the non-metallic elements (*e.g.*, oxygène, hydrogène, azote) were introduced.

Next came the binary substances, consisting, as they did, of two elements. The acids occurred in this class. Their

names were in each case composed of two words, of which the first was common to them all and indicated their acid character (*acide*), while the second was a specific name indicating the element or radical occurring in each. Thus we have '*acides sulfurique, carbonique, phosphorique, nitrique,*' etc. Two acids containing the same element or radical were distinguished by the different termination of the specific name; that containing the smaller proportion of oxygen receiving the termination '*eux,*' whereby such names as '*acides sulfureux, nitreux,*' etc., were obtained. Hydrochloric acid was called '*acide muriatique,*' and the existence of oxygen in it was assumed; while oxygen was supposed to be present in still greater quantity in chlorine—the '*acide muriatique oxygène.*'

The names of the binary substances of the second group—*i.e.*, of the basic compounds containing oxygen—were formed in a manner exactly similar. For these the general designation '*oxides*' was introduced, and to this word the specific name was appended in the genitive; for example, '*oxide de zinc,*' '*oxide de plomb,*' etc.

The remaining binary compounds were distinguished as sulphur, phosphorus, carbon, etc., compounds, and received the class names '*sulfures,*' '*phosphures,*' '*carbures,*' etc.

Compounds of the metals with one another were called '*alliages*' (alloys), the expression '*amalgames*' being retained, however, for mercury alloys.

With regard to the ternary compounds, the salts alone need be mentioned. They obtained their class names from the acids from which they were derived, and were called accordingly '*sulfates,*' '*nitrates,*' '*phosphates.*' The termination '*ate*' became '*ite*' when the salts were derived from the acid poorer in oxygen instead of from that richer in oxygen. The name of the base was appended; for example, '*sulfate de zinc, de baryte,*' etc.

This system of nomenclature embodies the principles and constitutes the basis of the chemical nomenclature now in use.

Studies of the new nomenclature were published by Scherer (1792), who made an attempt to Germanize the new terms; Eimbke (1793), who sought to reconcile the old and the new views in his synonymicon; Arzt (1795); Spalding, who published a work at Hanover, N. H., in 1799, in which he followed de Morveau, but adopted the name 'septon' for nitrogen and 'septic acid' for nitric acid, as proposed by Samuel Mitchell, of New York; Sevrin (1807); and Ritter (1808). It is amusing to note here that Richard Chenevix, a London chemist, published a critical examination of the nomenclature of the "French Neologists" in 1802, in which he quoted Balthazar Sage's remark that oxygen signified the "son of a vinegar merchant."

When the nature of the theoretical views held during the Phlogistic Period is compared with that of the ones accepted at the time of Lavoisier's execution, it will be understood why a new era—that of quantitative chemistry, or, as Fourcroy termed it, the "French Chemistry"—dates from him.

As mentioned, the teachings of Lavoisier gradually became recognized in France—a reward which Lavoisier himself had the satisfaction of witnessing—and also gained ground in England, and, through the influence of Klaproth, in Germany, where his works were translated, so that at the beginning of the nineteenth century chemists had almost universally given in their adherence to the antiphlogistic chemistry.

Lavoisier not only overthrew the old theory, but it is to his credit that he introduced a new one in its place, and it is perhaps advisable to state here the most important heads of his theory (Ladenburg):

1. In all chemical reactions it is the kind of matter alone that is changed, while its quantity remains constant; consequently, the substances employed and the products obtained may be represented by an algebraic

equation in which, if there is any unknown term, this may be calculated.

2. In the process of combustion the burning substance unites with oxygen, whereby an acid is usually produced. In the combustion of the metals, metallic calces are produced.

3. All acids contain oxygen, united, as he expresses it, with a basis or radical which, in inorganic substances, is usually an element, but in organic substances is composed of carbon and hydrogen, and frequently contains also nitrogen or phosphorus.

If these three statements be contrasted with the views of the phlogistians—*i.e.*, with the theories which prevailed prior to Lavoisier—we shall appreciate the reformation introduced by him into chemical science. The direction of chemical thought was entirely changed, and the facts hitherto ascertained appeared in a new light.

Chemistry now had the basis of a correct theory; and what was of greater value, a knowledge that theories could be deduced only from the weight relations of actually occurring reactions. To quote Venable, "There were to be no baseless and delusive dreams for the future, altho mistakes might be made in the interpretation of facts. Further, the grand division into elements and compounds had been effected, and a suitable nomenclature had been devised, capable of any expansion demanded by increase of knowledge. The balance, too, had been introduced as the instrument by which precision and accuracy were to be attained, and the great arbiter of the fate of theories. True progress now became possible; and the century which has since passed has seen this science develop and grow, until men have come scarcely to dare to put a limit to its possibilities."

Those three investigators—Guyton de Morveau, Claude Louis Berthollet, and Antoine François Fourcroy—who, in conjunction with Lavoisier, furnished the basis of a sci-

entific nomenclature, and also contributed to the development of chemistry by their other works, are next to be considered.

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equation in which, if there is any unknown term, this may be calculated.

2. In the process of combustion the burning substance unites with oxygen, whereby an acid is usually produced. In the combustion of the metals, metallic calces are produced.

3. All acids contain oxygen, united, as he expresses it, with a basis or radical which, in inorganic substances, is usually an element, but in organic substances is composed of carbon and hydrogen, and frequently contains also nitrogen or phosphorus.

If these three statements be contrasted with the views of the phlogistians—*i.e.*, with the theories which prevailed prior to Lavoisier—we shall appreciate the reformation introduced by him into chemical science. The direction of chemical thought was entirely changed, and the facts hitherto ascertained appeared in a new light.

Chemistry now had the basis of a correct theory; and what was of greater value, a knowledge that theories could be deduced only from the weight relations of actually occurring reactions. To quote Venable, "There were to be no baseless and delusive dreams for the future, altho mistakes might be made in the interpretation of facts. Further, the grand division into elements and compounds had been effected, and a suitable nomenclature had been devised, capable of any expansion demanded by increase of knowledge. The balance, too, had been introduced as the instrument by which precision and accuracy were to be attained, and the great arbiter of the fate of theories. True progress now became possible; and the century which has since passed has seen this science develop and grow, until men have come scarcely to dare to put a limit to its possibilities."

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sur les Lois de l'Affinité" (1801), and "Essai de Statique Chimique" (1803). The last-mentioned treatise was an exceedingly important contribution to theoretical chemistry, for it exerted a powerful influence on the question of chemical affinity. Berthollet's doctrine of affinity will be discussed in the next chapter.

Antoine François de Fourcroy (1755-1809) deserves mention as an organizer, author and teacher. He was an active expounder of the antiphlogistic doctrine, and propagated the new chemistry by means of articles and treatises. He was the author of the following works: "Leçons Élémentaires d'Histoire Naturelle et de Chimie" (1782), "Elémens d'Histoire Naturelle et de Chimie" (1789), "Mémoires et Observations de Chimie" (1784), "Philosophie Chimique" (1792), and "Système des Connaissances Chimiques et leurs Applications aux Phénomènes de la Nature et de l'Art" (1801). Fourcroy's experimental work served to pave the way for biological chemistry, and his joint investigations with Vauquelin furthered the knowledge of organic compounds.

Another important representative of chemistry in France at this time was Louis Nicolas Vauquelin (1763-1829), who succeeded Fourcroy as Professor of Chemistry to the Medical Faculty in 1809. To Vauquelin is owed the discovery of chromium (1797) and beryllia (1797), the former of which he found in lead spar and the latter in beryl. His work on the separation of platinum, palladium (discovered by Wollaston in 1803), rhodium (Wollaston, 1804), iridium (Tennant, 1803), and osmium (Tennant, 1803) is also worthy of note. Vauquelin's investigations on the metals of the platinum group were carried out with the assistance of Fourcroy, and it is likely that they preceded Smithson Tennant in the discovery of iridium. In his researches in organic chemistry, Vauquelin discovered quinic acid, asparagine, and camphoric acid. He was the author of two works—"Instruction sur la Combustion des Vegetaux, la Fabrication du Salin, de la

*Cendre Gravelee*" (1794), and "*Manuel de l'Essayeur*" (1812)—both of which passed through several editions.

The leading chemists of Great Britain and Sweden at the time when Lavoisier began his attack on the phlogistic theory strongly opposed the new chemistry. Cavendish, Priestley, Bergman, and Scheele were unable to accept it, but Black renounced the old doctrine in 1791, and was followed by Dickson and Richard Kirwan. The latter's interesting "*Essay on Phlogiston and the Constitution of Acids*" (1787) deals with the transition period from the old to the new theories, and was translated into French by Mme. Lavoisier. Among the lesser celebrities in the science in England, Lubbock subscribed himself to Lavoisier's views as early as 1784, while Peart and Pew attempted to prove the existence of phlogiston as late as 1795.

In 1810, a small '*Essay on Combustion*' was published in Philadelphia by a Mrs. Fulhame, "wherein the phlogistic and antiphlogistic hypotheses are proved erroneous." This is merely mentioned on account of its being one of the earliest American contributions to the subject.

Martin Heinrich Klaproth (1743-1817), first Professor of Chemistry at the University of Berlin, was characterized by the accuracy with which he carried out his investigations; the quantitative method of research was developed and improved by him, and he thereby helped on the recognition of the cardinal principles advocated by Lavoisier. After Klaproth had become satisfied with the correctness of the antiphlogistic doctrine, by testing the reactions which took place in combustion and calcination, he became one of its devoted adherents; and his example led many other German chemists in the same direction.

Klaproth discovered uranium (1789), titanium (1794), cerium (1803), and zirconia (1789); and investigated the new elements chromium, beryllium, and tellurium (discovered by Müller von Reichenstein in 1782). He was

particularly active in analytical and mineralogical chemistry, and introduced many improvements of analytical methods. Klaproth was, in fact, a true investigator in every sense of the word. In reporting the results of an analysis, he published the actual figures obtained, thus introducing a new custom which made it possible to subject results to correction or criticism. His works are "Chemische Untersuchung der Mineralquellen zu Karlsbad" (1790), and "Beiträge zur chemischen Kenntniss der Mineralkörper" (1795-1815). The latter is a collection of his papers published in the "Memoirs" of the Berlin Academy and in the "Chemische Annalen für die Freunde der Naturlehre." He also published the "Chemisches Wörterbuch" (1807-10, 5 volumes; 1815-19, 4 volumes), a French edition of which appeared in 1811; and edited the third edition of Friedrich Gren's "Systematisches Handbuch der Gesammten Chemie," an excellent treatise first published in 1787-90.

From 1803-10, Klaproth was on the board of editors of the "Neues allgemeines Journal der Chemie," which was started in 1798 by Scherer. In this connection it should be mentioned that at that time about twelve chemical periodicals were being published in Germany, three in France, two in Italy, two in Belgium, one each in Holland and Sweden, and two in England. These journals exercised the greatest influence upon the enlargement and diffusion of chemical knowledge, and they show the extent to which chemistry was fostered during the last decades of the eighteenth century.

## CHAPTER X

### THE ATOMIC THEORY AND THE WORK OF DAVY

A DESIRE ingenite in the human mind to find an explanation of natural phenomena, by the aid of speculations respecting the ultimate constituents of matter, resulted in guesses and ideas concerning atoms, in olden times, without, however, the evolution of an exact chemical atomic theory. With respect to the hypotheses of the ancient philosophers regarding the constitution of matter, the following estimate by Clifford will suffice in this connection:

"From the earliest times that men began to form any coherent idea of [the world] at all, they began to guess in some way or other how it was that it all began, and how it was all going to end. . . . Modern speculations are attempts to find out how things began and how they are to end, by consideration of the way in which they are going on now. . . . A great number of people appear to have been led to the conclusion that [the modern theory of the molecular constitution of matter] is very similar to the guesses which we find in ancient writers—Democritus and Lucretius. . . . It so happens that these ancient writers did hold a view of the constitution of things which in many striking respects agrees with the view which we hold in modern times. . . . The difference between the [ancient and modern views] is mainly this: the atomic theory of Democritus was a guess, and no more than a guess. Everybody around him was guessing about the origin of things, and they guessed in a great number of

ways; but he happened to make a guess which was more near the right thing than any of the others." \*

The conception of atoms had up to the close of the eighteenth century been almost entirely the property of the metaphysician and the mathematical physicist, and had assisted in extending their sciences. With the exception of Sennert and Boyle, chemists had aided little in its formulation and less in its establishment, nor had they derived inspiration from it for the proper founding of their own science. For more than a century they had been following the "ignis fatuus" of a false theory of combustion and a most elusive hypothetical phlogiston. The close of the eighteenth century found them engaged in bitter strife over these theories, and too fully occupied to think of much else than the destruction of the old beliefs and the adaptation of the new. The master mind of Lavoisier, who had wrought this revolution, was busied with the greater work of reconstruction and, dealing little with hypotheses which could not be directly proved by experiments in his laboratory, was laying broad and strong the foundations of the New Chemistry. Consequently the works of Bergman, Scheele, Priestley, Black, Cavendish, Macquer, and others do not treat of atoms and their moving forces, except in an occasional indefinite reference to some sort of particle.

Yet the chemist was the very one required to undertake the scientific development of the atomic hypothesis and to establish it as a theory, by discovering a series of facts which were connected together by it and found in it a simple explanation.

In 1783, the English chemist Kirwan went so far as to refer to affinity as that force which holds atoms so intimately together that simple mechanical means are insufficient to separate them; while his countryman, Higgins, writing in 1790 on the composition of sulphurous and sulphuric acids, expressed the opinion that the atom of sulphur is combined with one atom of oxygen in the first, but with two atoms in the second. It is in view of this state-

ment, and others similar to it, that some have regarded Higgins as the real originator of the modern atomic doctrine. However, Higgins restricted his attention to a small number of compounds. His conceptions were not consistent with fact; he regarded those weights of elements which combine to form the simplest compound as in general equal; and he made no attempt to seek confirmation for any theory he had in the laboratory. For long the common consent of public opinion has given the undivided honor, due to the discoverer of the great atomic generalization in its modern aspect, to John Dalton.

Before the establishment of the chemical atomic theory could be brought to completion, however, it became necessary to fix the signification of the term "chemical proportions," according to which simple substances unite to form compound bodies; and an important part of this question was solved by two chemists prior to Dalton—Richter and Proust.

Jeremias Benjamin Richter (1762-1807) published in his "*De usu Matheseos in Chymia*" (1789), "*Aufangsgründe der Stöchiometrie oder Messkunst Chymischer Elemente*" (1742-1794), and "*Ueber die neuen Gegenstände der Chymie*" (1791-1802), the results of researches made mainly while employed as a works chemist in Berlin. The last two mentioned treatises contain the conclusions which he drew from his work upon the proportions by weight in various compounds.

Richter looked upon chemistry as a branch of applied mathematics, and exhibited all the distressing qualities of a person possessed by a fixed idea; he spent his life in seeking arithmetical regularities in the weights of acids and alkalis neutralizing each other, and in finding them in spite of their non-existence.

Nevertheless, he managed to make discoveries of the highest importance. He not only noticed, but also correctly interpreted the fact, that when two neutral salts decompose one another, the resulting salts are still neu-



tral. To quote his conclusions: "... concerning that very common experience that two neutral salts on decomposition again produce neutral compounds, I could draw no direct inference other than that fixed quantitative relations must exist between the constituents of the neutral salts. If a solution of two components is so constituted that neither of them, as long as it remains in the solution, exhibits the peculiar characteristics it had before solution—*e.g.*, the reactions of an acid or of an alkali—then such a solution is called saturated or neutral, or also a neutral compound. . . . When two neutral solutions are mixed and a decomposition ensues, the newly formed products are also, almost without exception, neutral. . . . Hence it follows that if the combining ratios in the original compounds be known, those in the newly formed compounds are known also."

C. F. Wenzel (1740-1793), at an earlier date (1777), had demonstrated that acids and bases combine in constant proportions, but had failed to note the persistency of the neutrality in the double decomposition of the neutral salts.

Richter deduced from the maintenance of neutrality when one metal precipitates another from a neutral solution—a relation Bergman had observed, but which he interpreted in terms of another theory—that the quantities of two metals which dissolve in the same amount of acid also unite in their oxides with the same amount of oxygen. Therefore, he established that quantities of two substances which are equivalent in one reaction are also equivalent in others; he was the originator of stoichiometry, or "the art of chemical measurement, which has to deal with the laws according to which substances unite to form chemical compounds."

Notwithstanding the fact that Richter's treatise contained such important discoveries these remained unrecognised until Fischer published a table of the relative affini-



ties of bases and acids, founded on the values Richter had obtained, in his translation of Berthollet's "Recherches," made in 1802.

Berthollet accepted the law of proportionality and gave an account of it in his "Essai de Statique Chimique," in which he reprinted Fischer's note. Thus Richter's work, which at the time of its publication had been almost completely ignored, became more widely known and appreciated.

Louis José Proust (1755-1826), altho a Frenchman by birth, conducted his most important researches in Madrid, where he settled after 1791. The work for which he is celebrated was the result of a series of questions which Berthollet had advanced.

The two works of Berthollet on affinity—"Recherches sur les Lois de l'Affinité" and "Essai d'une Statique Chimique"—were particularly directed against false views of affinity and the misuse of the so-called affinity tables of Geoffroy, Bergman, and others.

He contended that affinity was by no means a simple force, and easy to determine or measure; but was influenced by temperature, physical state, cohesion, and especially by mass. The latter largely determined the course of chemical reactions.

He went further, however, and from the correct premise of the influence of mass on the chemical effect produced, Berthollet drew the erroneous inference that mass had an influence, not only on the amount of change but also on the kind, producing a continuous variation in the ratio in which the constituents are united in the compound. He asserted the variability of the composition of chemical compounds, the possibility of combination between constituents in all sorts of continuously varying ratios. None of the other leading chemists of the day were able to concur with his views as to the lack of any fixity or constancy of proportions in chemical compounds. Yet

they raised no objection, probably owing to Berthollet's reputation, and it remained for Proust to attack the theoretical conclusions of his eminent contemporary.

Proust's numerous papers in his controversy with Berthollet appeared in the "Journal de Physique" between the years 1802 and 1808. The lucidity of the arguments employed, the variety of the experimental work described, and the freedom and keenness of the style, render these papers, which deal exclusively with the distinctly dry subject of quantitative analysis, most interesting reading even now.

Proust proves that substances formed under the most varied conditions have a fixed composition, and he shows that Berthollet's examples of variable composition were all cases of mixtures. This involves him in the necessity of discriminating between mixtures and compounds, an undertaking the difficulties of which he fully realized, and with which he dealt in a manner very much like that still resorted to for the same purpose.

In 1799, Proust had proved the constant composition of native and artificial carbonate of copper, and had enunciated the general principle of which this constituted an example. Of greater importance than these were observations he made upon the two compounds iron forms with sulphur and the two stages of oxidation shown by tin. He further investigated the compounds of antimony, cobalt, nickel, and copper, and throughout he found that, vary the conditions and relative masses at pleasure, the oxides and sulphides produced always have a definite composition. To be sure, an element might combine with oxygen or sulphur in two proportions, but each was a compound of definite proportions.

Proust showed the error which underlay the old method of determining the quantity of oxygen in oxides, of estimating the metal and calculating the oxygen by difference, proving that in many cases the bodies so examined were not oxides at all, but compounds containing hydrogen—

hydroxides we now call them. He, moreover, demonstrated that many of the bodies, on the analysis of which Berthollet had based his generalization, were not simple at all, but mixtures of substances, themselves of perfectly definite composition. So accurate were his analytical investigations, and so logical his reasoning, that Berthollet was overcome at every point. The law of definite chemical proportions, as we now have it, was the fruit of his persevering labors. This law is one of the fundamental principles of chemistry. It is expressed by the greatest teacher of chemistry as follows:

"If one substance is transformed into another, then the masses of these two substances always bear a fixed ratio to each other. If several substances react together, then their masses, as well as those of the new bodies formed, always bear fixed proportions to each other." (Ostwald, "Outlines of General Chemistry.")

Undoubtedly, if Proust had calculated the results of his experiments on the composition of binary compounds (sulphides, oxides) in another manner from what he did, he would have discovered the law of multiple proportions, but the propounding of this is due to Dalton.

John Dalton (1766-1844) was born at Eaglesfield, in Cumberland, the son of a poor weaver; endowed with natural aptitude and an indomitable will, he utilized all possible opportunities for the study of mathematics and natural philosophy. From 1781 to 1793 he taught school, instructed and lectured at Kendal, devoting all the time and energy he could spare to scientific investigations, chiefly meteorological.

In 1793 he went to Manchester as tutor of mathematics and natural philosophy at a Presbyterian College. Tho he resigned this post six years later, he remained in Manchester to the end of his life, earning his living as a private teacher, and devoting himself uninterruptedly and earnestly to scientific research.

The earlier researches of Dalton on the expansion of gases by heat and their absorption by liquids were of considerable influence on his later chemical work, as it was through them that he acquired the experimental skill which led to the discovery of the law of multiple proportions, which, with the conception of the atomic theory which arose from it, dates from 1802.

On November 12, 1802, Dalton read a paper entitled "An Experimental Enquiry into the Properties of the Several Gases or Elastic Fluids constituting the Atmosphere," in which is found the first example of the law. In determining the amount of oxygen in the air the following experiment was performed:

"If 100 measures of common air be put to 36 of pure nitrous gas in a tube  $\frac{3}{16}$  of an inch wide and 5 inches long, after a few minutes the whole will be reduced to 79 or 80 measures, and exhibit no signs of either oxygenous or nitrous gas. If 100 measures of common air be admitted to 72 of nitrous gas in a wide vessel over water, such as to form a thin stratum of air, and an immediate momentary agitation be used, there will, as before, be found 79 or 80 measures of pure azotic gas [nitrogen] for a residuum. If, in the last experiment, less than 72 measures of nitrous gas be used, there will be a residuum containing oxygenous gas; if more, then some residuary nitrous gas will be found. These facts clearly point out the theory of the process: the elements of oxygen may combine with a certain portion of nitrous gas, or with twice that portion, but with no intermediate quantity. In the former case nitric acid is the result; in the latter nitrous acid: but as both these may be formed at the same time, one part of the oxygen going to one of nitrous gas, and another to two, the quantity of nitrous gas absorbed should be variable; from 36 to 72 per cent. for common air."

With regard to this experiment Roscoe says: "In the memorable case in which Dalton announces the first in-

stance of combination in multiple proportions the whole conclusion is based upon an erroneous experimental basis. If we repeat the experiment, as described by Dalton, we do not obtain the results he arrived at. We see that Dalton's conclusions were correct, altho in this case it appears to have been a mere chance that his experimental results rendered such a conclusion possible."

The first of the observations of Dalton which furnished the experimental basis for the atomic theory consisted in the determination of the composition of two hydrides of carbon. Dalton writes: "It was in the summer of 1804 that I collected at various times and in various places the inflammable gas [marsh gas] obtained from ponds." He found that marsh gas, like olefiant gas (ethylene), contains nothing but carbon and hydrogen, and that these two substances, termed light and heavy carburetted hydrogen, respectively, showed a simple multiple ratio between the weights of the constituent elements, namely:

In carburetted hydrogen from stagnant water, 4.3 of carbon were combined with 2 of hydrogen.

In olefiant gas, 4.3 of carbon were combined with 1 of hydrogen.

This regularity induced him to investigate other compounds in the same direction; thus, in the case of carbonic oxide and carbonic acid he found that, for the same amount of carbon, the ratios of oxygen present in these were again, respectively, as 1:2. His conviction that there must be a law underlying these simple relations scarcely necessitated any further accretion after he had encountered similar simple numerical proportions in the results of his analysis of nitrous oxide, nitric oxide, nitrous acid and nitric acid—i.e., the anhydrides of the two last—and the oxygen compounds of sulphur. He had, therefore, demonstrated that when different quantities of one element combined chemically with one and the same quantity of another, these amounts stood in a simple relation to one another—a relation which could be expressed by

whole numbers. The "law of multiple proportions" was thus discovered; it had, indeed, been deduced from experiments which were of necessity not very exact, but this was to be expected from the condition of analytical chemistry at that time.

Dalton next sought an explanation of the numerical relations he had discovered, and this was afforded him by the atomic hypothesis. For instance, he had but to assume that in carbon monoxide one atom of carbon was combined with one of oxygen, and in carbonic acid one atom of carbon was united to two of oxygen. Upon this basis Dalton erected his Atomic Theory, which may be detailed from statements in his "New System of Chemical Philosophy" (1808-1810), as follows:

1. All bodies of sensible magnitude are constituted of a vast number of extremely small particles or atoms of matter bound together by a force of attraction, which, as it endeavors to prevent their separation, is called attraction of cohesion; but as it collects them from a dispersed state is called attraction of aggregation, or, more simply, affinity.

2. The ultimate particles of all homogeneous bodies are perfectly alike in weight, figure, etc. In other words, every particle of water is like every other particle of water, every particle of hydrogen is like every other particle of hydrogen, etc.

3. No new creation or destruction of matter is within the reach of chemical agency. All the elements we can produce consist in separating particles that are in a state of cohesion or combination and joining those that were previously at a distance.

4. The ultimate particles of all simple bodies are atoms incapable of further division. These atoms (at least viewed along with their atmospheres of heat) are all spheres, and are possessed of particular weights which may be denoted by number.



5. If there are two bodies which are disposed to combine, then their combination takes place by atoms.

6. In an elastic gas each particle occupies the center of a comparatively large sphere and supports its dignity by keeping all the rest, which by their gravity, or otherwise, are disposed to encroach upon it, at a respectful distance.

The method by which Dalton determined the relative atomic weights from the proportions by weight in which the elements unite to form compounds, falls next to be described.

To accomplish this the first thing necessary was to settle the number of atoms in a compound. According to Dalton, this number is to be sought for, in general, in the simplest possible ratios. In estimating it, he started from the following principles:

1. When only one compound of two elements is known, this is composed of an atom of the second order.

2. When two compounds are known, the one consists of an atom of the second and the other of an atom of the third order.

3. When three compounds are known, one atom of the second and two atoms of the third order must be assumed.

How did Dalton now proceed to the determination of the atomic weights—*i.e.*, the relative weights of the smallest particles? In the first place it was necessary to choose a unit for comparison. As unit he assumed hydrogen with the atomic weight = 1, and he referred all the other atomic weights to this. To fix the others, he then applied his first principle. At that time only one compound each of oxygen and of nitrogen with hydrogen was known, *viz.*, water and ammonia, respectively; therefore, the atomic weights of oxygen and nitrogen can be determined directly from the composition of these compounds. In this way Dalton found them to be 7 and 5, respectively. He checked the numbers so obtained by the proportions of the oxygen and nitrogen in the oxygen compounds of nitrogen. He was acquainted with four of the latter. In



nitric oxide he found 7 parts of oxygen for 5 of nitrogen; its atom was, therefore, the atom of the second order, derived from these elements. In nitric acid, according to his view, there were 14 parts of oxygen for 5 of nitrogen, or two atoms of the former gas for one of the latter. In nitrous oxide, 7 parts of oxygen were combined with 10 parts of nitrogen, and in this he therefore assumed two atoms of nitrogen and one of oxygen. Nitrous acid, however, is supposed to contain  $10\frac{1}{2}$  parts of oxygen for 5 of nitrogen, and in it he might have assumed two atoms of nitrogen and three of oxygen. He preferred, however, to regard this substance as a compound of nitric acid and nitric oxide.

Likewise, he found in ethylene 5.4 parts of carbon for 1 of hydrogen, and in marsh gas the same quantity of carbon for 2 of hydrogen. On this account he regarded ethylene as consisting of atoms of the second order, and assumed the atomic weight of carbon to be 5.4. Carbonic oxide likewise consisted of atoms of the second order, since he found in it 7 parts of oxygen for 5.4 of carbon, while carbonic anhydride had atoms of the third order, because it contains 14 parts of oxygen for 5.4 of carbon.

As the analytical methods Dalton employed were liable to many sources of error, it was out of the question that the results he obtained could be accurate. However, he it was who propounded the principle of the determination of the combining weights of the elements, and this work brought him everlasting fame.

Dalton's atomic theory, generally speaking, was favorably received by chemists. Thomas Thomson (1773-1852), who founded the first chemical laboratory for general instruction in Great Britain while professor in the University of Glasgow, became its devoted supporter, and his "System of Chemistry" (1807) made it known to the general public. In 1808, Thomson supplied an observation of his own in support of the law of multiple proportions.

To quote his own inference:

"It appears that there are two oxalates of strontian, the first obtained by saturating oxalic acid with strontian water, the second by mixing together oxalate of ammonia and muriate [chloride] of strontian. It is remarkable that the first contains just double the proportion of base contained in the second." He also investigated the potash salts of oxalic acid.

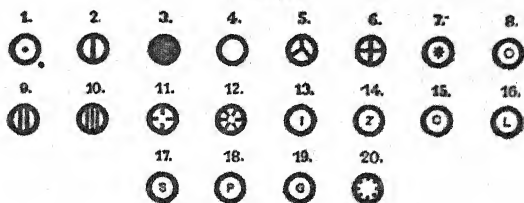
"Oxalate of potash readily crystallizes in flat rhomboids, commonly terminated by dihedral summits. The lateral edges of the prism are usually beveled. At the temperature of  $60^{\circ}$  it dissolves in thrice its weight of water. . . . This salt combines with an excess of acid and forms a super-oxalate, long known by the name of salt of sorrel. The acid contained in this salt is very nearly double of what is contained in oxalate of potash. Suppose 100 parts of potash; if the weight of acid necessary to convert this quantity into oxalate be  $x$ , then  $2x$  will convert it into super-oxalate."

Similar research was done by W. H. Wollaston (1766-1828), who, by experiment, found that in the two compounds termed "subcarbonate of potash" and "carbonate of potash," the proportions of carbonic acid relatively to the same amount of potash were as 1:2. He also showed that "super-sulphate" (bisulphate) of potash contains "exactly twice as much acid as is necessary for the mere saturation of the alkali present." These contributions proved the applicability of the law for salts, and the importance of the relation thus made evident was, in general, realized by the chemists of the day.

Dalton's attempts at a graphic presentment of the ultimate particles of various substances must not be forgotten. The symbols he used to represent the atoms of the elements and to indicate the constitution of chemical compounds, as well as his relative weight values, are here given. This system of notation never came into general use owing to the introduction of a simpler system by Berzelius some time afterward.

Fig.	Rel. wt.	Fig.	Rel. wt.
1. Hydrogen .....	1	11. Strontites .....	46
2. Azote .....	5	12. Barytes .....	68
3. Carbone or Charcoal .....	5	13. Iron .....	38
4. Oxygen .....	7	14. Zinc .....	56
5. Phosphorus .....	9	15. Copper .....	56
6. Sulphur .....	13	16. Lead .....	95
7. Magnesia .....	20	17. Silver .....	100
8. Lime .....	23	18. Platina .....	100
9. Soda .....	28	19. Gold .....	140
10. Potash .....	42	20. Mercury .....	167
21. An atom of water or steam, composed of 1 of oxygen and 1 of hydrogen, retained in physical contact by a strong affinity, and supposed to be surrounded by a common atmosphere of heat. ....			8
22. An atom of ammonia, composed of 1 of azote and 1 of hydrogen.....			6
23. An atom of nitrous gas, 1 azote + 1 oxygen.....			12
24. An atom of olefiant gas, 1 carbone + 1 hydrogen..			6
25. An atom of carbonic oxide, 1 carbone + 1 oxygen.			12
26. An atom of nitrous oxide, 2 azote + 1 oxygen..			17
27. An atom of nitric acid, 1 azote + 2 oxygen.....			19
28. An atom of carbonic acid, 1 carbone + 2 oxygen			19
29. An atom of carburetted hydrogen, 1 carbone + 2 hydrogen .....			16
30. An atom of oxynitric acid, 1 azote + 3 oxygen..			26
31. An atom of sulphuric acid, 1 sulphur + 3 oxygen			34
32. An atom of sulphuretted hydrogen, 1 sulphur + 3 hydrogen .....			16
33. An atom of alcohol, 3 carbone + 1 hydrogen....			16
34. An atom of nitrous acid, 1 nitric acid + 1 nitrous gas .....			31
35. An atom of acetous acid, 2 carbone + 2 water...			26
36. An atom of nitrate of ammonia, 1 nitric acid + 1 ammonia + 1 water.....			33
37. An atom of sugar, 1 alcohol + 1 carbonic acid...			35

**ELEMENTS**  
Simple



**Binary**



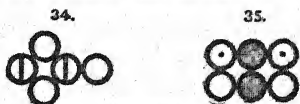
**Ternary**



**Quaternary**



**Quinquenary and Sextenary**



**Septenary**

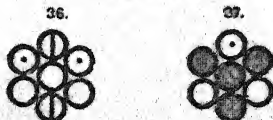


Fig. 20 --DALTON'S GRAPHIC PRESENTMENT OF THE ELEMENTS.

It is now necessary to discuss the position which Davy and Gay-Lussac, among others, held respecting Dalton's atomic theory, as well as to narrate their services to chemistry in general.

Humphrey Davy, the son of an engraver, was born at Penzance in 1778. The family circumstances were somewhat impecunious, and at the age of seventeen he was apprenticed to a surgeon-apothecary in his native town.

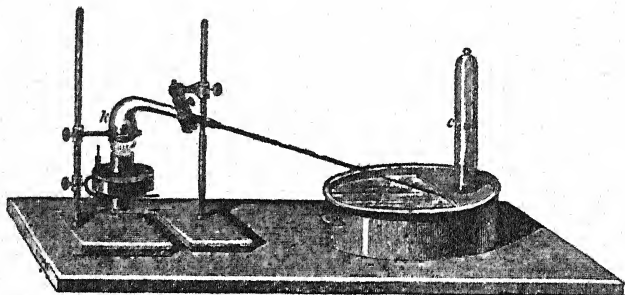


Fig. 21 — PREPARATION OF NITROUS OXIDE.

At the age of twenty he was placed in charge of the laboratory of the Pneumatic Institute at Bristol, founded by Beddoes for the application of gases to the treatment of diseases. Davy's environments here were most propitious for a successful career of scientific research. His laboratory was well furnished, and was supported by the subscriptions of scientific men. He had plenty of time at his disposal, and the age was one of discovery and rapid progress in the science. His experiments related chiefly to nitrogen monoxide, or nitrous oxide, and in a short time he published his "Researches Chemical and Philosophical, chiefly concerning Nitrous Oxide and its Respiration." His courage and his determination were well

proved by these experiments. The effects of this gas, supposed to be poisonous, were tried upon himself. He discovered its anesthetic action. He then subjected himself similarly to the action of hydrogen, nitrogen, and carbonic acid. In 1801, Davy left Bristol to become a lecturer at the Royal Institution, and two years later was elected Fellow of the Royal Society. He was soon a necessary figure in the fashionable life of the day; his auditors at the Royal Institution were numbered by the thousand; his name was on everybody's lips. It was Coleridge who said, "I attend Davy's lectures to increase my stock of metaphors." He was knighted in 1811 and created baronet in 1812. A terrible mining disaster at Felling brought him an invitation from the governors of the mine to investigate the conditions of such occurrences, and after an extended investigation into the nature of marsh gas in its different admixtures with air, he projected his well-known safety lamp. This is but one instance out of many of his scientific insight being turned to material advantage. Davy was elected President of the Royal Society in 1820, and died at Geneva in 1829.

At the Royal Institution Davy had at his command an excellent electric battery, and, as he had for some time considered that the most-needed step in chemistry was the decomposition of some of the substances then regarded as elementary, he thought that this was the most promising means for the solution of the question.

In 1790 Galvani made his well-known experiment, and ten years later Volta invented his electric cell. These were important elements in the inquiry which went to correlate chemical and electrical phenomena, and the perception that a close relation existed between electrical force and chemical reaction spread rapidly at the beginning of the nineteenth century, after the decomposition of water into its constituents by the galvanic current had been proved by Nicholson and Carlisle (in 1800), and that of salts into their bases and acids by Berzelius and Hisinger



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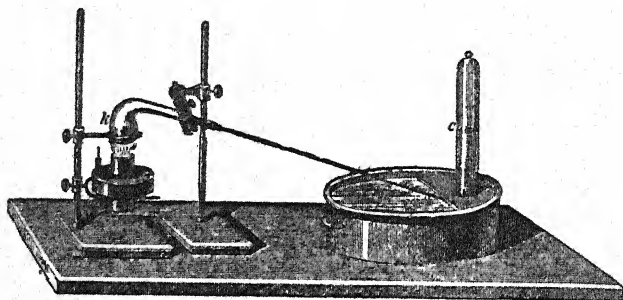


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(in 1803). The most important of the many and varied observations on the department of chemical compounds when subjected to the action of the current, however, were made by Davy, and his discoveries entitle him to be regarded as the pioneer of electrochemistry, as well as one of the most brilliant chemists the world has ever seen.

Davy was among the first to investigate the question of the decomposition of water. This work was begun in 1800. In his Bakerian lecture delivered before the Royal Society in 1806, the subject of which was, "On Some Chemical Agencies of Electricity," is found an investigation concerning the products of the electrolysis of water. Besides hydrogen and oxygen there were also formed acid and alkali. Davy states this as a fact:

"The appearance of acid and alkaline matter in water acted on by a current of electricity at the opposite electrified metallic surfaces was observed in the first chemical experiments made with the column of Volta."

The problem requiring solution then was to ascertain whether the acid and alkali were derived from the water, and if not, whence they came. Davy therefore proceeded to carry out this electrolysis in vessels of various materials, and showed that the products mentioned, the acid and alkali, were due to the glass, or to the matter dissolved in the water, or to the air itself. If the water, distilled in silver, was electrolyzed in gold vessels, in an atmosphere of hydrogen, the acid and alkali did not appear. To give his own description:

"I repeated the experiment under more conclusive circumstances. I arranged the apparatus as before [gold cones and water distilled in silver vessels]; I exhausted the receiver and filled it with hydrogen gas from a convenient air-holder; I made a second exhaustion and again introduced hydrogen that had been carefully prepared. The process was conducted for twenty-four hours, and at the end of this time neither of the portions of the water altered in the slightest degree the tint of litmus. It seems

evident then that water chemically pure is decomposed by electricity into gaseous matter alone, into oxygen and hydrogen."

He next investigated the decomposition of salt solutions, and found confirmation of the statements of Berzelius and Hisinger. But he proceeded with still greater circumspec-

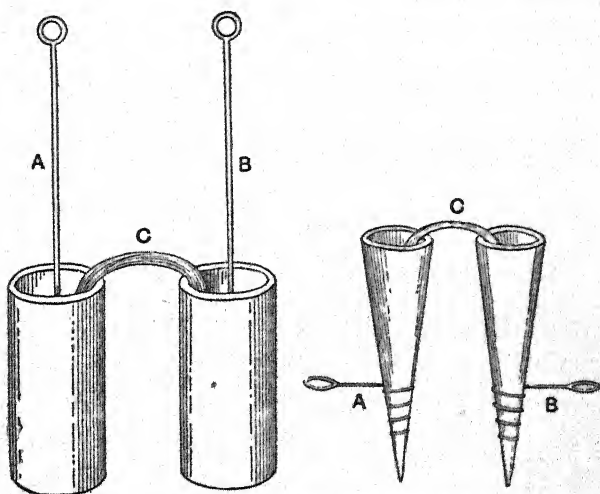


Fig. 22 —DAVY'S APPARATUS FOR ELECTROLYSIS OF WATER.  
A. and B., electrodes; C., strand of asbestos.

tion, and sought to follow up the phenomena more exactly. All the means were at his command, and he did not hesitate to avail himself of them.

Direct observation proved to Davy that hydrogen, the alkalies, the metals, etc., are separated by means of the current at the negative pole, and oxygen and the acids at the positive pole. From this he concluded that the former substances possess a positive, while oxygen and the acids

possess a negative electrical energy; that in this case, as usual, the oppositely electrified bodies attract each other; and that, in consequence, the positive substances separate at the negative pole, and vice versa. In this assumption Davy had arrived at an explanation of the phenomena of decomposition observed in the galvanic circuit. But he proceeded a step further, and endeavored to refer all chemical combination and decomposition to similar causes.

According to him the heat observed in certain cases of decomposition were manifestations of electricity.

On November 19, 1807, Davy delivered an account to the Royal Society of his most recent work on the nature of the alkalies. He had made an attempt to decompose them by the electrolysis of their aqueous solutions, but without success; he had then passed a powerful current through solid potash fused over a flame, and had observed a most intense light at the negative pole, due probably to the combustion of the element he was seeking. And his next experiment was decisive; to give his own description: "A small piece of pure potash, which had been exposed for a few seconds to the atmosphere, so as to give conducting power to the surface, was placed upon an insulated dish of platina, connected with the negative side of a powerful battery, . . . the positive pole was brought in contact with the upper surface of the alkali. On passing the current, the potash began to fuse at both its points of electric action. There was violent effervescence at the upper surface; at the lower or negative surface there was no liberation of elastic fluid, but small globules having a high metallic luster appeared." And he had treated soda in the same manner with similar results. "It appears," he said, "that in these facts there is evidence for the decomposition of potash and soda into oxygen and two peculiar substances." To these two peculiar substances he gave the names potassium and sodium.

In 1808, Davy had decomposed hydrochloric acid by means of potassium, and in this way had obtained hydro-

gen and potassium chloride, the latter of which he had also prepared by burning potassium in chlorine. He proved, in 1809, that the chlorides (muriates) of the metals are not decomposed by heating them with calcium metaphosphate or with silicic anhydride, but that decomposition at once begins when aqueous vapor is conducted over the mixture. Davy considered that Henry's hypothesis furnished the explanation of these experiments, and that hydrochloric acid could only be separated as soon as the quantity of water necessary for its existence was supplied.

About the same time Gay-Lussac and Thénard showed that water is produced as well as silver chloride by the action of this acid upon silver oxide; and, as formerly, they assumed that this water was already present in the hydrochloric acid. They then effected the synthesis of the acid, by exposing a mixture of chlorine and hydrogen to sunlight. On this occasion, they advanced a complete theory regarding hydrochloric acid and chlorine, by means of which they were able to explain all their experiments. According to them, hydrochloric acid was a compound of an unknown radical, "muriaticum," with oxygen and water; chlorine, on the other hand, was anhydrous hydrochloric acid combined with more oxygen.

Davy next sought to find the oxygen which was assumed to be present in "oxymuriatic acid," but by no means whatever could he abstract the oxygen from this compound; a succession of electric sparks produced no effect, neither did strongly ignited carbon. If the gas were oxidized, muriatic acid, phosphorus and sulphur might be expected to combine with the oxygen and liberate the muriatic acid; no such result had been obtained, however, and the oily liquids which were produced only yielded muriatic acid on the addition of water. The "oxymuriatic acid," when passed over oxides of potassium, barium, and other metals, produced "muriates" with evolution of precisely that amount of oxygen contained in the oxides. Referring to

this experiment, Davy remarks, "It is contrary to sound logic to say that the exact quantity of oxygen is given off from a body not known to be compound, when we are certain of its existence in another." He therefore explained these facts by regarding "oxidized muriatic acid" as an elementary substance, and muriatic acid as its compound with hydrogen; but chemists hesitated about accepting his views. Davy maintained that this element, to which he gave the name "chlorine," resembled oxygen in many respects, and, in a limited sense, was also to be regarded as an acidifier and supporter of combustion.

The work of Davy was clear and brought conviction, and by 1820 his theory of the nature of chlorine was generally accepted. But oxygen could no longer be regarded as the sole acid-making principle, and this necessitated a new theory of acids.

A French saltpeter manufacturer, Courtois, in 1811 discovered a peculiar substance in the soda obtained from sea plants; he related his observation to Clément, who showed the body in question to Davy. Davy soon demonstrated its elementary nature, and Gay-Lussac, after a complete investigation of iodine, as he termed it, and its compounds, succeeded in showing its marked likeness to chlorine. Bromine was discovered by Balard, in 1826, in the mother liquor of sea-water. Hydrofluoric acid resisted all attempts to isolate its radical, but Ampère's suggestion that it was constituted similarly to muriatic acid found general acceptance.

From his observation that iodic anhydride was devoid of acid properties, but acquired them after combination with water, Davy arrived at the conclusion that hydrogen and not oxygen was the acidifying principle in the latter compound; hydrogen, in his opinion, was an essential constituent of all acids. The assumption that hydrated acids and salts contained water or metallic oxides together with acid anhydrides, he held to be unproven and unnecessary.

The French chemist Dulong expressed himself in a



like manner after an investigation of oxalic acid and its salts; the former he looked upon as a compound of hydrogen with carbonic acid, while in the latter he assumed an analogous combination of the metals with the elements of carbonic acid.

The principles of a new theory of acids was, therefore, included in the discussions of Davy and Dulong, but it is to be deplored that they did not follow them up sufficiently, as otherwise they might have prevented the distinction which now began to be drawn between acids containing oxygen and those which did not.

With regard to Davy's attitude to the atomic theory of Dalton, it should first be mentioned that he asserted in 1809 that William Higgins was the originator of this doctrine. The latter's "A Comparative View of the Phlogistic and Antiphlogistic Theories with Inductions" (1789), Davy maintained, contained views similar to those of Dalton; but later he recognised Dalton's service.

Davy regarded Dalton's atomic weights as simply the proportion numbers of the elements, and maintained that there was no positive basis upon which to proceed for the determination of the atomic weights. Two other investigators of this time—Wollaston and Gay-Lussac—also refused to admit that Dalton's atomic weights were really such. Previous to Davy, Wollaston had asserted that these were the chemical equivalents of the elements, while Gay-Lussac would only concede that the ratio of one element to another was fixed by analytical and synthetical determinations. His law of combining volumes had a definite bearing on the atomic theory, however, and this generalization, along with his work in analytical chemistry and numerous researches in inorganic chemistry, render further notice of him necessary.

Joseph Louis Gay-Lussac (1778-1850) was a student of Berthollet, and in 1809 became professor of chemistry at the Ecole Polytechnique, at the same time holding the chair of physics at the Sorbonne. In 1832, he accepted the



chair of chemistry at the Jardin des Plantes. Gay-Lussac was a masterly investigator, capable of the most accurate analytical work and exact in observation, and enriched chemistry with many valuable researches. Of especial importance was his work on iodine and its compounds; on cyanogen, which he characterized as the first compound radical; on sulphur and its compounds; on the oxides of nitrogen; on the isolation of boron; and his conjoint investigations with L. J. Thénard on the alkali metals, and with Liebig on the fulminates. He also introduced improved methods of inorganic and organic analysis, and is to be regarded as having laid the foundations of volumetric analysis. His name is particularly associated, however, with his investigations on the combining volumes of gases.

In 1805, Gay-Lussac and Alexander von Humboldt published a memoir entitled "Experiments on the Ratio of the Constituents of the Atmosphere," in which they announced that they had found the volume ratio, hydrogen: oxygen:: 200: 100. This led Gay-Lussac to extend his investigations to the volume relations of other gaseous substances which are compounds of gaseous constituents, and by the close of the year 1808 he was able to announce results which showed the existence of a simple and general law. He summarized his results as follows:

"I have shown in this memoir that the compounds of gaseous substances with each other are always formed in very simple ratios, so that representing one of the terms by unity, the other is one, or two, or at most three. These ratios by volume are not observed with solid or liquid substances, nor when we consider weights, and they form a new proof that it is only in the gaseous state that substances are in the same circumstances and obey regular laws. . . . The apparent contraction of volume suffered by gases on combination is also very simply related to the volume of one of them, and this property likewise is peculiar to gaseous substances."

This law of combining volumes is stated by Ostwald in his "Outlines of General Chemistry" as follows:

"If gaseous substances enter into chemical combination, their volumes are in simple rational proportions, and if a gaseous substance is formed by their union, its volume also is rationally related to the volumes of the original gases."

Gay-Lussac was himself inclined to conjoin his law of volumes with the atomic theory—indeed, he recognised in it a support for the latter. A similar molecular condition was essential, however, in order that all gases should deport themselves alike toward pressure and changes of temperature, and, besides, obey his law of volumes. In other words, equal volumes of gases must contain equal numbers of molecules. Gay-Lussac drew no distinction between these molecules and atoms, recognizing but one kind of final particle. Dalton opposed this reasoning, and stated that he had held the same view as to combining volumes at one time, but finally saw that it was untenable. To quote from his "A New System of Chemical Philosophy":

"At the time I formed the theory of mixed gases I had a confused idea, as many have, I suppose, at this time, that the particles of elastic fluids are all of the same size; that a given volume of oxygenous gas contains just as many particles as the same volume of hydrogenous. But . . . I became convinced that different gases have not their particles of the same size; and that the following may be adopted as a maxim till some reason appears to the contrary, namely:

"That every species of pure elastic fluid has its particles globular and all of a size; but that no two species agree in the size of their particles, the pressure and temperature being the same."

He also maintained that gases do not combine exactly by volumes, but frequently by fractions of volumes. He said: "The truth is, I believe, that gases do not unite in

equal or exact measures in any one instance; when they appear to do so, it is owing to the inaccuracy of our experiments. In no case, perhaps, is there a nearer approach to mathematical exactness than in that of one measure of oxygen to two of hydrogen; but here the most exact experiments I have ever made gave 1.97 hydrogen to 1 oxygen."

His argument may be illustrated as follows, taking hydrochloric acid as an example:

One atom of hydrogen chloride consists of one atom of hydrogen and one atom of chlorine. Then, if equal volumes of gases contain equal numbers of molecules, one volume of hydrogen and one volume of chlorine should produce one volume of hydrogen chloride, but they really form two. Consequently, each one of these can contain only half as many atoms as the original volumes of the constituents. Such ratiocination is manifestly conclusive so far as the theory of the volumes containing the same number of atoms is concerned, unless some different definition of atoms is assumed.

The connection between Gay-Lussac's law of volumes and Dalton's atomic theory was shown by the Italian physicist Amadeo Avogadro (1776-1856) in 1811.

Avogadro discarded Dalton's artificial distinction between the ultimate particles of a compound and those of an element, and made a distinction between what he termed "molecules integrants" and "molecules elementaires," or molecules and atoms, the former being compound particles made up of the indivisible atoms. The researches of Gay-Lussac indicate, then, that a molecule of water consists of one molecule of hydrogen and one-half molecule of oxygen. A molecule of hydrogen chloride consists of one-half molecule of hydrogen and one-half molecule of chlorine, and so the difficulty pointed out by Dalton was effaced from chemical literature.

Avogadro's assumption that "equal volumes of gases,

elementary or compound, at the same temperature and pressure contain equal numbers of molecules," altho only a hypothesis, is generally referred to as "Avogadro's Law." It is of fundamental importance to chemistry. He also stated that the relative weights of gaseous molecules may be determined by measurement of the relative weights of equal volumes of the gaseous substances—that is, by comparison of gaseous densities; and that the number of gaseous volumes interacting indicates the relative number of molecules interacting, and similarly the volume of the compound gas formed when compared with that of the constituents gives the number, whole or fractional, of elementary molecules entering into the composition of one compound molecule.

Avogadro's conclusions produced practically no effect at the time they were promulgated, and fifty years passed by before they were received with due recognition. These conclusions of Avogadro are sometimes credited to the French mathematician Ampère (1775-1836), but the memoir of the latter did not appear until 1814, and is much less important than that of Avogadro.

While Davy and Gay-Lussac were conducting their valuable investigations, an important literary-chemical event, most impressive and attractive in nature, occurred when William Prout (1785-1850) advanced his hypothesis of the genesis of the elements.

In 1815, in a paper upon the relations between the specific gravities of bodies in the gaseous state and their atomic weights, Prout stated that he had often observed the close approximation to round numbers of many of the weights of the atoms. From the table at his command he further deduced that all elementary numbers, hydrogen being considered as 1, are divisible by 4, except carbon, nitrogen and barium, and these are divisible by 2, appearing, therefore, to indicate that they are modified by a higher number than unity or hydrogen. He considered

the other number might be 16, or oxygen, and that possibly all substances were composed of these two elements.

A short time after, in 1816, he expressed the following views: "If the views we have ventured to advance be correct, we may almost consider the *πρώτη ὕλη* of the ancients to be realized in hydrogen, an opinion, by the by, not altogether new. If we actually consider this to be the case, and further consider the specific gravities of bodies in their gaseous states to represent the number of volumes condensed into one, or, in other words, the number of the absolute weights of a single volume of the first matter (*πρώτη ὕλη*) which they contain, which is extremely probable, multiples in weight must always indicate multiples in volume and *vice versa* and the specific gravities or absolute weights of all bodies in a gaseous state must be multiples of the specific gravity or absolute weight of the first matter, because all bodies in a gaseous state, which unite with one another, unite with reference to this volume."

Prout's conjecture was taken up by Thomas Thomson, who, being carried away by the attraction of simplicity, became the advocate of a philosophical speculation contrary to experimental facts, and even perceived in it a fundamental law of chemistry. Other chemists, too, showed a predilection for "Prout's Hypothesis," and, notwithstanding the fact that Berzelius and Turner demonstrated its untenability, some exact investigators as late as 1840 betrayed an inclination to some of Prout's views. In fact, some writers of the present day consider that there may be a kernel of truth concealed in it, and, altho it has suffered numerous reversals, it is still revived at intervals.

## CHAPTER XI

### BERZELIUS AND THE DEVELOPMENT OF THE ATOMIC THEORY

COMPLETE success had rewarded the exertions of Lavoisier, and, through the efforts of Proust, Richter, Dalton, Gay-Lussac, and Davy, the spirit of order was creeping in on all sides, but it was exceedingly fortunate for chemistry that an investigator with the sense of coördination that Berzelius possessed should have made his advent just at this time, when laws required confirmation and theories nourishment. The foundations of the new system required extension and generalization, and how opportune was the appearance of one who could illumine the whole domain of chemistry. Berzelius ruled as an autocrat for over a quarter of a century, and the modern chemist can hardly over-extol his obligation to him.

Jons Jakob Berzelius was born at Wäfversunda, in Ostergötland, Sweden, on August 20th, 1779. His father was a schoolmaster in Linköping, and died four years after the birth of his son, who for some time afterward had to endure many privations.

Berzelius studied medicine at Upsala, and subsequently practiced, but he had early acquired a devotion to chemistry and kept in close touch with it. He was but twenty when he undertook his first extensive chemical research—an investigation of the medicinal springs at Medevi, in the neighborhood of his birthplace. A short time after, in 1802, in conjunction with Hisinger, he commenced the examination of the action of the electric current on vari-



ous salts, with the most far-reaching results for chemistry and for himself; for almost immediately the desire to keep so promising a student in Stockholm induced the authorities to create for him a new academic position, that of assisant professor of medicine, botany and pharmacy at the University of Stockholm.

In 1807, he was installed in the chair of medicine and pharmacy, and also taught chemistry at the Military College from the year 1806. In 1815, he accepted the chair of chemistry in the Chirurgico-Medical Institute of Stockholm, where he accomplished the researches which made him famous, and where his lectures enabled him to impress his views upon the rising generation of chemists. Among his pupils may be mentioned Heinrich and Gustav Rose, Mitscherlich, Wöhler, Christian Gottlob Gmelin, Magnus, Mosander, Svanberg and Sefström.

From the year 1818, when he was nominated permanent secretary to the Stockholm Academy, of which he had been a member since 1808, and more particularly after 1832, when Mosander succeeded him in his chair, Berzelius devoted himself to literary work with a subservience which has hardly been equaled from a utilitarian standpoint by any chemist either before or after him. He died on the 7th of August, 1848.

Berzelius was an exceptional observer, and a most accurate and operose investigator, exhibiting very close attention to details. It is difficult to render an account of his achievements, as they extended over almost the entire field of chemistry and produced reforms of great importance.

And one must not forget that the laboratory in which Berzelius accomplished his famous researches was small and imperfectly equipped. To give Wöhler's description of his first visit to it:

"No water, no gas, no hoods, no oven, were to be seen; a couple of plain tables, a blowpipe, a few shelves with bottles, a little simple apparatus, and a large water-barrel



whereat Anna, the ancient cook of the establishment, washed the laboratory dishes, completed the furnishings of this room, famous throughout Europe for the work which had been done in it. In the kitchen which adjoined, and where Anna cooked, was a small furnace and a saribath for heating purposes."

Berzelius introduced many improvements in analytical chemistry. It was he who first employed far smaller amounts of substances than the large quantities recommended by Klaproth, who introduced the spirit-lamp which bears his name, thereby rendering the incineration of filter-paper and the ignition of precipitates facile, and who worked out many new methods of analysis. Among the latter were his plan of decomposing silicates by the aid of chlorine. He enriched mineralogy by many analyses of minerals and mineral waters, and in a number of these—*e.g.*, those of platinum ores—he devised new methods of separation.

Berzelius was the first to characterize minerals as being in every respect "chemical compounds," and he classified them similarly to substances prepared artificially. He was also able to demonstrate that the doctrine of chemical proportions, and consequently the atomic theory, was applicable to minerals.

The close attention which Berzelius gave to details resulted in the discovery of selenium (1817), thoria (1828), and, in conjunction with Hisinger and independent of Klaproth, he discovered ceria (1803). He also discovered many new chemical compounds, among which were the compounds of selenium with hydrogen and oxygen, and some molybdenum compounds; isolated the elements silicon (1810), zirconium, and tantalum (1824); and extended the knowledge of the platinum metals.

Passages in the works of Berzelius indicate that he regarded the firm establishment of the doctrine of chemi-

cal proportions, and, in conjunction with this, the determination of the atomic weights of the elements and the constitution of chemical compounds, as his main task. To quote from his "Lehrbuch der Chemie," fifth edition:

"I resolved to make the analysis of a number of salts whereby that of others might become superfluous. . . . I soon convinced myself by new experiments that Dalton's numbers were wanting in that accuracy which was requisite for the practical application of his theory. . . . I recognised that if the newly arisen light was to spread, it would be necessary to ascertain with the utmost accuracy the atomic weights of all elementary substances, and particularly those of the more common ones. Without such work, no day would follow the dawn. This was therefore the most important object of chemical investigation at the time, and I devoted myself to it with unrelenting labor. . . . After work extending over ten years . . . I was able in 1818 to publish a table which contained the atomic weights, as calculated from my experiments, of about 2,000 simple and compound substances."

In the years 1812 to 1816, Berzelius investigated the stages of oxidation of most of the metals and metalloids then known, and, by determining the composition of these oxides, confirmed the law of multiple proportions. His analytical work greatly surpassed that of Dalton, and in the rules established for his guidance in deciding the number of atoms in a given compound or molecule, he exhibited a greater knowledge; still, his rules were, in some respects, arbitrary and unsatisfactory.

He took oxygen = 100 as his standard, giving as his reason for this preference the following:

"To refer the other atomic weights to that of hydrogen offers not only no advantages, but has, in fact, many inconveniences, seeing that hydrogen is very light and is seldom a constituent of inorganic compounds. Oxygen, on the other hand, unites all the advantages in itself. It is, so to speak, the center-point round which the whole

of chemistry revolves." This view is, again, at the present time held by many chemists, who take 16 as the atomic weight of oxygen, and base the atomic weights of all the other elements upon this number.

Berzelius began his work at the time when Wollaston was attempting, by his use of the term equivalents, to eliminate the question of atoms. Thomson was employing the standard oxygen = 1, considering that this number would give more of the atomic weights as whole numbers, and failing to perceive that the law of volumes had any particular significance from the atomic standpoint.

Berzelius, however, perceived in the law of volumes a corroboration of the atomic theory, and allowed himself to be guided by it in his views upon the number of atoms in chemical compounds, and, consequently, upon the numerical values of the atomic weights. His "volume theory" contained the attempt to combine Gay-Lussac's law with the atomic theory. He set forth the atomistic view, which he had himself put into shape under the influence of the law of volumes, definitely and conclusively in two papers. He started with the assumption that in the case of every simple substance, when it was in the gaseous form, one volume corresponded with one atom, and, therefore, made use of the designation "volume atoms" for those smallest particles. Wherever it was practicable, he attempted to measure the volumes of the combining substances, and from these deduced the atomic numbers. The analysis of the compound, in which the volumes of the elementary constituents were known, led him to the true determination of the atomic weights of the latter. For example, from the fact that water consists of two volumes of hydrogen and one of oxygen, he deduced the atomic composition of water which holds at the present day, together with the relative atomic weights of oxygen and hydrogen; and from the mode of formation of carbonic oxide and carbonic acid he arrived at the true composition

of these compounds, and at the atomic weight of carbon, and so forth.

Still, the use which Berzelius made of Gay-Lussac's law was too limited to free him from the necessity of employing rules for deciding the number of atoms in compounds.

In 1818, Berzelius gave a table of atomic weights which contained values which compare favorably with those of other observers. Nine years later he published another table which brought his atomic weights still closer to those now current.

The reason given by Berzelius for halving in 1826 many of the atomic weights assigned to the metals in 1818 was as follows:

"It is known that the oxide of chromium contains three atoms of oxygen. Chromic acid for the same number of chromium atoms contains twice as much oxygen, which would be six atoms; but in its neutral salts chromic acid neutralizes an amount of a base containing one-third as much oxygen as it contains itself, a relation found to hold in the case of all acids with three atoms of oxygen—*e.g.* sulphuric acid and sulphates. In order to harmonize the multiple relation between the amount of oxygen in the oxide and in the acid, it is most probable that the acid contains three atoms of oxygen to one atom of chromium, and the oxide three atoms of oxygen to two of chromium. Isomorphous with the oxide of chromium are those of manganese, iron and aluminium; these also we know to contain three atoms of oxygen, and consequently must represent them as containing two atoms of the radicle. But if the ferric oxide consists of  $2\text{Fe} + 3\text{O}$ , the ferrous oxide is  $\text{Fe} + \text{O}$ , and the whole series of oxides isomorphous with it contains one atom of the radicle and one atom of oxygen."

Thus we see that E. Mitscherlich's law of isomorphism—that compounds of analogous composition and containing the same number of atoms crystallize in the same crystalline form—announced in 1819, and which Berzelius re-

garded as "the most important since the establishment of the doctrine of chemical proportions," was an aid in testing his atomic weight determinations, for, according to him, isomorphism indicated similarity in atomic constitution.

Berzelius further showed that with the exception of cobalt and silver the law of specific heat justified the change made in 1826. This law was advanced in 1819 by P. L. Dulong and T. A. Petit, who, in investigating the specific heats of the metals and other bodies, reached the important conclusion that these were very nearly inversely proportional to their atomic weights. Multiplied by their atomic weights, the specific heats gave a constant quantity. This resulted in the law as stated by them: the atoms of the different elements have the same capacity for heat. It is not difficult to perceive that by means of the specific heat one could readily approximate to the true atomic weight, and arrive at a decision as to which of two or more possible figures represented the true weight.

There were exceptions to the law which have been explained only in late years. However, the law was extended to simple chemical compounds, and proved of great assistance after it was more fully understood. Berzelius opposed the acceptance of it at first, in part, because it would necessitate a revision of his table of atomic weights, and might endanger the accepted views as to some of the atomic relations. He gradually gave up this position, however, when the law was confirmed by other workers, and more accurate determinations were made than the first ones of Dulong and Petit.

Berzelius substituted for Dalton's geometrical symbols a more convenient system of chemical notation, which, to give his own words, "might facilitate the expression of chemical proportions, show briefly and clearly the number of elementary atoms in each compound, and after the determination of their relative weights, present the results

of each analysis in a simple and easily retained manner." The atom of each element was represented by the initial letter of its Latinized name, a second letter being added when two elements had names beginning with the same capital. An index number was added when more than one atom was present.

A compound was thus represented by placing the proper number of these symbols side by side. Thus, H is hydrogen, Cl is chlorine, and HCl is hydrogen chloride. Berzelius assumed the existence of certain double atoms (where two atoms of an element occur together). These were indicated by a mark across the symbol; thus H with a stroke through it, followed by O, was water, or, as it is now written,  $\text{H}_2\text{O}$ . For convenience' sake, an atom of oxygen was often indicated by a point or dot, thus:

Carbon Dioxide,  $\ddot{\text{C}}$ ; "Nitrous Acid,"  $\ddot{\text{N}}$ ; Potassium Nitrate,  $\text{K}\ddot{\text{N}}$ .

These symbols were a great advance over those suggested by Dalton, which were diagrammatic and quite impractical. Dalton, however, criticized the system of notation of Berzelius, saying that "Berzelius' symbols are horrifying; a young student in chemistry might as soon learn Hebrew as make himself acquainted with them."

Berzelius adopted dualism as the basis of his chemical system. He extended the term atom so that it included what he regarded as compound atoms, which were built up of two parts, each of which might be a simple atom or several atoms, in which each of the two parts acted as a single simple atom. This was the dual structure, which dominated all of his views with regard to chemical phenomena, and for more than a decade held a preëminent position in chemistry. Berzelius seemed to have formed this idea of dualism from his observations upon the volumes of gases. For a certain number of these gases the equivalent is formed of two atoms. This was true not



only of hydrogen, but of nitrogen, chlorine, and others, in the form of vapor. The atomic weights of these bodies represent also the specific gravities, or the weights of one volume compared with one volume of the standard; but since it requires two volumes of nitrogen, two volumes of chlorine, etc., to form the first stage of oxidation with oxygen, two volumes of nitrogen, etc., represent the equivalents of these bodies compared with oxygen. Berzelius considered that these atoms, therefore, were united two and two, and called them the double or compound atoms.

A uniform method of considering compounds dualistically became possible to a still greater degree in the light of electro-chemical phenomena, and Berzelius introduced this into chemistry and established it.

Davy had inclined to the assumption that electrical processes and the phenomena of chemical affinity arose from a common cause. His electro-chemical theory was characterized by the axiom that the small particles of substances which have an affinity for one another only become oppositely electrified upon contact. The researches of Berzelius, however, caused the abandonment of this principle, while otherwise many of Davy's original ideas were retained. Davy advanced ideas as to the manner in which he considered chemical and electrical phenomena to be related, but he never succeeded in producing a theory which might serve as the basis of a chemical system. This was accomplished by Berzelius, and therefore his views are of greater importance in the development of chemistry than those of Davy are. To quote from A. Ladenburg's "Lectures on the History of Chemistry":

"According to Berzelius, it is not only when two substances are brought into contact that electricity is generated, but it is a property of matter; and in every atom, two oppositely electrical poles are assumed. These poles do not, however, contain equal quantities of electricity. The atoms are unipolar, the electricity of the one pole predominating over that of the other; and thus every atom



(and therefore every element) appears to be either positively or negatively electrical. In this respect it is possible to arrange the elementary substances into a series, so that each member is always more electro-negative than the next succeeding one. Oxygen stands at the top and is absolutely electro-negative, while the other substances are only relatively positive or negative according as they are compared with elements which come before them or after them in the electrical series. This series does not constitute a table of affinities in the Geoffroy-Bergman sense; and it does not express the affinity of the individual substances for oxygen, for example. Berzelius has not forgotten Berthollet's teaching, that affinity is not of a constant character and independent of the physical conditions, as he supposes this unipolarity to be; and he is also well aware that oxygen can be removed from metallic oxides by carbon or sulphur—that is to say, by other electro-negative substances. With him, affinity depends principally upon the intensity of the polarity—i.e., upon the quantity of electricity which is contained in the two poles." This is variable, however, especially with changes of temperature, and, generally speaking, is increased by furnishing more heat, which explained why certain combinations only occurred at a high temperature.

Chemical combinations of the elements or compounds consisted, according to Berzelius, in the attraction of the dissimilar poles of the small particles and in the consequent neutralization of the different electricities. When positive electricity predominated in the original substance, then an electro-positive compound resulted, and vice versa. If the electricities neutralized one another, then an electrically indifferent product was the result. Oxygen, as the most electro-negative element, served Berzelius here as the standard by which to determine the kind of polarity of the various elements. Those elements which yielded basic compounds with oxygen, even altho only their lowest oxides were basic, were classed as electro-positive, and those

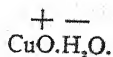
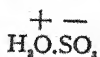
whose oxides were acids as electro-negative. Following this principle he arranged the simple substances in a series, in which oxygen as the first member was followed by the other metalloids, while hydrogen formed the bridge between the latter and the metals, the whole ending with sodium and potassium.

Such conceptions formed the substance of his electro-chemical theory, which constituted the basis of the dualistic theory of chemical composition. Berzelius established it as follows:

"If the electro-chemical views are accurate, it follows that every chemical combination depends wholly and solely upon two opposite forces, namely, the positive and the negative electricities, and that every compound must be composed of two parts, united by the effects of their electro-chemical reactions, since there is not any third force. From this it follows that every compound substance, whatever the number of its constituents may be, can be divided into two parts, of which the one is positively and the other is negatively electrical. Thus, for example, sulphate of soda is not composed of sulphur, oxygen, and sodium, but of sulphuric acid and soda, each of which can, in turn, be separately divided into an electro-positive and an electro-negative constituent. In the same way, also, alum cannot be regarded as immediately composed of its elementary constituents, but is to be looked upon as the product of the reaction of sulphate of alumina, as negative element, with sulphate of potash, as positive element; and thus the electro-chemical view justifies what I have said with respect to compound atoms of the first, second, third, etc., orders."

In the year 1819, when Berzelius contributed a complete exposition of his electro-chemical theory, he was convinced that all acids contained oxygen. In his view water assumed in hydrated acids the rôle of a weak electro-positive constituent, and in metallic hydroxides that of a

weak electro-negative one; the hydrates of sulphuric acid and of cupric oxide, therefore, received the formulæ—



The binary conception, which had already been applied by Lavoisier to acids and bases, and even by Rouelle to salts, thus received the strongest support from the electro-chemical theory, and was materially developed as a result.

Finally, however, the theory of the oxygen acids, based on the tenet established by Lavoisier, was abandoned by chemists during the second decade of the nineteenth century, as a knowledge of facts in opposition to it augmented, and at last Berzelius convinced himself of the existence of acids free from oxygen, at which time the unadaptable system of dualism began to decline in favor. It had explained, however, the mysterious chemical force, even tho the identification of chemical affinity with electrical polarity was one not justified by the facts at hand, and dominated chemistry for two decades.

As a result of the efforts of Berzelius, chemistry was now in the possession of a comprehensive theory of chemical reaction, a rational and systematic nomenclature, and a large quantity of experimental data. He was responsible for a solid basis in the laws of constant proportions and multiples, and the table of atomic weights which he published in 1827 was remarkably accurate, the determinations approaching the more exact work of the present time. These contributions equipped chemistry for the period of remarkable extension in the accumulation of data and in the formulation of theory which the past eighty years have witnessed.

Mention has been made of the law of Dulong and Petit and of the law of Mitscherlich. The exceptions to the former, exhibited by many of the non-metals in a greater or lesser diminution of the atomic heats, have only in

some measure been explained in recent years by the proof that the specific heats of such elements vary greatly with the temperature. In the case of simple chemical compounds, a relation was soon found between their specific heats and atomic weights by Neumann in 1831, who said:

"I find that for compound substances a simple relation exists between the specific heats and the stoichiometric quantities; and I call stoichiometric quantities the amounts of substances which, as for instance in the case of the anhydrous carbonates, contain the same amount of oxygen, while in the case of sulphur compounds the amount of sulphur is the measure of the stoichiometric quantity. For chemically similar substances the specific heats are inversely proportional to the stoichiometric quantities; or what comes to the same thing, the stoichiometric quantities of chemically similar substances have the same heat capacity. The investigation of the carbonates first led me to the discovery of this law."

Regnault, who extended the empirical basis of the law of constant atomic heat in 1840, while engaged in investigations on the specific heats of compounds corroborated Neumann's result, but it was reserved for Kopp in 1865 to definitely prove that the connection between the specific heat and the composition of a compound holds in the perfectly simple and general manner enunciated by Petit and Dulong, and that heat capacity is of the nature of an additive property.

The law of Mitscherlich was the outgrowth of coördinating physical form with chemical composition, a question which, until the time of Eilhard Mitscherlich (1794-1863), had been attacked entirely from the crystallographic side.

In 1801, Abbé Haüy (1743-1822), the founder of the science of crystallography, produced a system of mineral classification based first on their crystalline character, and secondly on their chemical composition. His guiding prin-

ciple was that every difference in the fundamental form of a crystal implied difference in its chemical composition.

This supposed law was supported by numerous facts, but there were also on record well-defined and undoubted exceptions. As far back as 1772, Romé de l'Isle had observed that copper sulphate and ferrous sulphate crystallize from a mixed solution in the form of the latter, and in 1788 Klaproth established the chemical identity of rhombohedral calcite and rhombic aragonite.

Mitscherlich was the first to recognise definitely the relation between crystalline form and chemical constitution. He explained the occurrence of isomorphous crystals in substances of different nature by demonstrating that they possessed a similar chemical composition. For instance, he found, on examining the salts of phosphoric and arsenic acids, that only those of analogous composition and containing equal amounts of water of crystallization were isomorphous. His subsequent investigations of selenates and sulphates, of the isomorphism of magnesium and zinc oxides, and of iron, chromium and aluminium salts, confirmed the intimate connection existing between crystalline form and chemical composition. Primarily, after making those observations, Mitscherlich was of opinion that isomorphism depended chiefly on the number of the elementary particles, but he soon became convinced that the chemical nature of these had also to do with it.

The importance of Mitscherlich's work met with immediate recognition, and data in support of the law were quickly accumulated. With regard to its deductive application, it is employed for purposes of classifying the elements and of atomic weight determinations. From the isomorphism of the salts of an acid of selenium with sulphates and chromates, Mitscherlich was led to the discovery of that acid (selenic acid); and his recognition of the isomorphism with potassium sulphate of the green potassium salt of a manganese acid, and of the isomorphism with potassium perchlorate of the red potassium salt of

another manganese acid, has revealed the true composition of these two acids.

It has been mentioned how the isomorphism of sulphates and chromates induced Berzelius to modify the formula of basic chromic oxide and to a subsequent halving of the atomic weights of most of the metals. He still adhered to the idea that the amounts of the elements contained in equal gaseous volumes were proportioned to their atomic weights. However, this assumption was soon invalidated by the remarkable results of an investigation which exercised such a marked influence on the views of many chemists that it must be described at this point.

This was the work of Jean Baptiste André Dumas (1800-1884) on the atomic weights. In 1827, Dumas published a paper entitled "Memoir on some points of the atomistic theory," in which he stated that "The object of these researches is to replace by definite conceptions the arbitrary data on which nearly the whole of the atomic theory is based."

Dumas showed that the conception of the equivalent cannot be employed as the basis of a system, because it loses its significance when it is extended further than to acids, to bases, and to other substances which closely resemble each other (oxides and sulphides); and, particularly, that it becomes quite obscure when the attempt is made to identify the equivalent with the combining weight, since very many substances can combine in several proportions. For example, 8 parts of copper are combined with 1 part of oxygen in cuprous oxide, while for 8 parts of copper, 2 parts of oxygen are contained in cupric oxide. Calculated from these numbers, the equivalent of copper, referred to that of oxygen as unity, is 8 or 4.

In order to confirm his ideas, Dumas adopted Avogadro's hypothesis as a basis, and devised in 1827 an admirable method for the determination of vapor densities.

He considered that the determination of the density of vapors and gases, elementary as well as compound, was



necessary to elucidate the question of the composition of the elementary molecule. But his practice did not agree with his theory; he and his contemporaries argued from the premise that the vapor densities of elements are proportional not only to their molecular weights, but also to their atomic weights, which of course involved the unwarranted assumption that all elementary gaseous molecules are composed of the same number of atoms—*i.e.*, of two.

He was successful in elaborating a method for conducting determinations of this kind at high temperatures, and used it for ascertaining the relative densities of the vapors of iodine, phosphorus, sulphur, mercury, etc. His results, from which he anticipated confirmation of his views, induced him to abandon them. He found the density of phosphorus vapor to be twice as great, and that of sulphur vapor to be three times as great as he had previously assumed, while that of mercury vapor was only one-half of what he had supposed. In view of these facts he began to doubt; in fact, he declared that even the simple gases do not contain, in the same volume, the same number of chemical atoms. According to him, the assumption could still be made that there is the same number of molecular or atomic groups present in equal volumes of all gases; but that this is only a hypothesis, which cannot be of service. Dumas was obliged to admit that Gay-Lussac's law, when applied in the way he had applied it to the determination of atomic weights, furnished erroneous results. Hence he believed that it could not be employed for this purpose, and he abandoned Avogadro's hypothesis.

Berzelius also was able no longer to maintain the law of volumes so far as its application in atomic weight determinations was concerned, and confined his proposition to the permanent gases.

The reform which Dumas had aimed at was, therefore, without result, and, if anything, he had merely introduced obscurity into the atomic weight system of Berzelius.



As a result, chemists regarded Avogadro's law with indifference. The law of Dulong and Petit was shown also to have some unexplained exceptions, and Mitscherlich, by his further discovery of dimorphism, had thrown much doubt upon his law of isomorphism. Consequently, at the close of the thirtieth year of this century the atomic theory was regarded by many chemists as either disproved or excluded to a very hypothetical position.

Even Gay-Lussac and Liebig doubted whether it was possible to determine the relative weights of the atoms with certitude, and would have left the atomic weights out of consideration, substituting the establishment of equivalents. Leopold Gmelin, however, was at the head of the movement to supplant the system of Berzelius by the equivalents of Wollaston.

According to Gmelin, there was no strict distinction between mixtures and compounds, and this demonstrates that he did not believe in the real existence of atoms. Two substances, especially when they possess only a weak affinity for each other, can combine, according to him, in an infinite number of proportions; but the greater the affinity, the greater is their tendency to combine in few proportions only. These proportions then stand to each other in simple relations. "There can, therefore, be assigned to every substance a certain weight in which it combines with definite weights of other elements. This weight is the stoichiometric number, the chemical equivalent, the mixture weight or atomic weight, and so on. Compounds are composed in such proportions that one mixture weight of one substance is united to  $\frac{1}{4}$ ,  $\frac{1}{3}$ ,  $\frac{1}{2}$ ,  $\frac{2}{3}$ ,  $\frac{3}{4}$ , 1,  $1\frac{1}{2}$ , 2,  $2\frac{1}{2}$ , 3, 4, 5, 6, 7, or more mixture weights of the other." According to Gmelin, Gay-Lussac's law runs as follows: "One measure of an elastic fluid substance combines with 1,  $1\frac{1}{2}$ , 2,  $2\frac{1}{2}$ , 3,  $3\frac{1}{2}$ , and 4 measures of the other."

Gmelin's table of equivalents is well known. It ran:  $H = 1$ ,  $O = 8$ ,  $S = 16$ ,  $C = 6$ , etc. Water was written  $HO$ , and in formulæ generally the attempt was made to

replace by simplicity what they had lost in conception and in purpose. As Ladenburg observes, "Chemistry was to become a science of confined observation—indeed almost to description alone. Skill in manipulation was all that was required; speculation was banished as dangerous.

"It had come to this, then: Inorganic chemistry, in connection with physics, had not been able to maintain the conception of the atom."

By the assistance of the growing science of organic chemistry, however, the theories of chemistry were rescued and advanced, and the atomic theory was reintroduced. But reference must be made to the status of the atomic theory in England at this time.

In England in the 1833 edition of Edward Turner's "Elements of Chemistry" the atomic theory is referred to as follows:

"In consequence of the satisfactory explanation which the laws of chemical union receive by means of the atomic theory it has become customary to employ the term atom in the same sense as combining proportion or equivalent."

A discovery of great importance was made in 1834, when Michael Faraday (1794-1867), professor in the Royal Institution of London, who had been engaged in studying quantitatively some changes produced by the passage of a current of electricity, detected the connection which existed with the combining numbers of the elements, and thereby deduced his law of electrical equivalents.

Faraday made the observation that the same galvanic current decomposed electrolytes—*e.g.*, water, hydrochloric acid and metallic chlorides—in such a manner that equivalent amounts of hydrogen or metal were separated at the negative pole, and the corresponding quantities of oxygen or chlorine at the positive. He classified those facts together under the title of "The Law of definite Electrolytic Action." In the determination of electro-chemical equivalents he perceived a sure auxiliary means for adjusting chemical atomic weights in doubtful cases.

## CHAPTER XII

### THE DEVELOPMENT OF ORGANIC CHEMISTRY

LAVOISIER showed that organic substances were composed principally of carbon, hydrogen, and oxygen, together with nitrogen, and sometimes sulphur and phosphorus. He had observed that an element was capable of forming more than one oxide, and from this he concluded that organic radicals deported themselves similarly. He consequently regarded sugar as the neutral oxide "d'un radical hydro-carboneux," and oxalic acid as its higher oxide. He even hazarded the conjecture that the fatty oils, which he considered to be hydrocarbons, might actually constitute organic radicals in the free state, and might, by oxidation, be converted into neutral oxides and vegetable acids.

Among Lavoisier's other investigations in organic chemistry, his research on the process of vinous fermentation is worthy of mention. He expressed the results in the form of the equation—

3 oz. 7 gros of water + 2 lbs. 8 oz. sugar produce, on fermentation,

1 lb. 7 oz. 5 gros 18 grains of alcohol + 1 lb. of carbonic acid.

"In this equation," says he, "there is only sugar whose constitutional parts are unknown to me. I know the composition of water, of alcohol, and of carbonic acid, and nothing is easier than to substitute these values in the equation established and then deduce the constituent parts of sugar."

However, Lavoisier did not regard organic chemistry as a separate division of the science. He classed all acids together, and, like Lemery (1675), subdivided them into mineral, vegetable, and animal acids. With a few exceptions, the immediate followers of Lavoisier followed the same plan, and the division of chemistry into inorganic and organic chemistry was not generally adopted until it became clear that several compounds occur both in the vegetable and animal kingdom, and therefore that no difference existed between vegetable and animal chemistry. In this connection the work of M. E. Chevreul (1786-1889) should be emphasized, as it was his investigations which demonstrated that many of the fats and acids and other substances, occurring in both kingdoms, were identical.

However, for some time subsequently considerable doubt prevailed as to the boundary of inorganic and organic chemistry. One reason for this was that inorganic substances, as well as some which had to be considered as organic, gave on analysis numbers which demonstrated that their composition was in accordance with the laws of constant and multiple proportions. As Berzelius stated in 1811, the majority of organic substances, however, appeared not to obey these laws, and consequently he undertook to decide this question by the analysis of a large number of them. After years of labor, and after improving the appliances and methods of organic analysis, he finally obtained results which proved that altho most organic compounds possessed a much more complicated composition than the mineral compounds, yet they obeyed the laws of constant and multiple proportions. He adopted the views of Lavoisier, and said (Schorlemmer):

"After we have got a clearer insight into the difference existing between the products of organic and inorganic nature, and the different manner in which their ultimate components are united with each other, we find this difference consists really in the fact that in inorganic nature

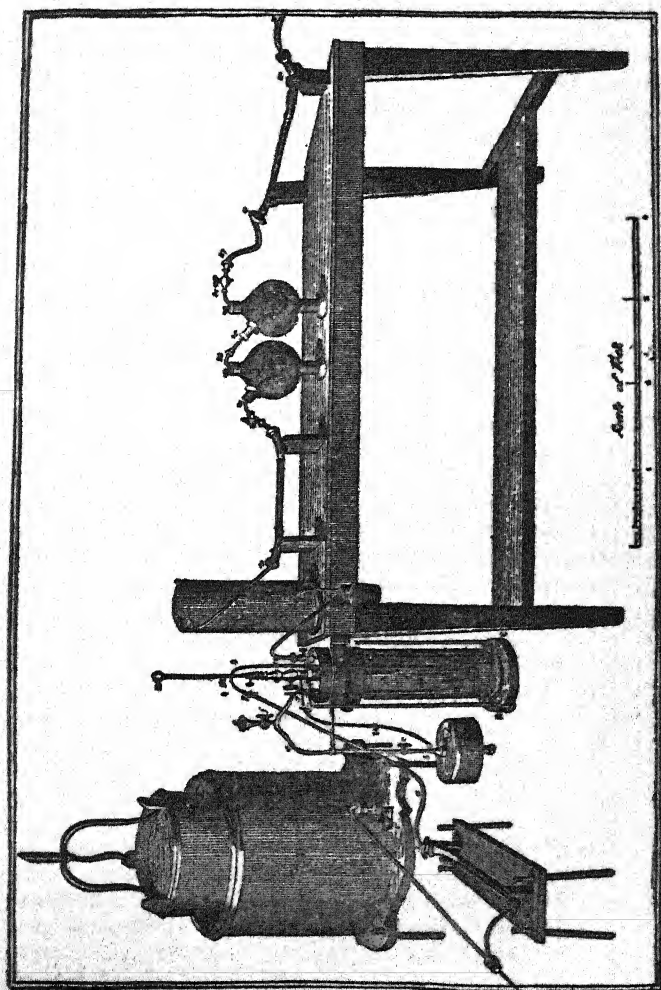


Fig. 23 --LAVOISIER'S APPARATUS FOR THE ANALYSIS OF ORGANIC SUBSTANCES.

all oxidized bodies contain a 'simple radical,' while all organic substances are 'oxides of compound radicals.' The radicals of vegetable substances consist generally of carbon and hydrogen, and those of animal substances of carbon, hydrogen, and nitrogen."

In his ideas as to these radicals he was especially influenced by the research of Gay-Lussac upon cyanogen, in which he showed that this radical played the rôle of an element. Attempts were multiplied to discover the various organic substances having complex groupings of atoms which performed as elements. Thus, Gay-Lussac regarded alcohol as ethylene and water. Döbereiner considered oxalic acid as carbonic acid and carbon monoxide. As Berzelius pointed out, this was opposed to the electro-chemical theory, and there was danger of confusion and error.

The search for the proximate constituents in organic substances induced a rapid development of the science, leading especially to many efforts at definitely determining the chemical constitution of these bodies. One of the most important of the discoveries in the third decade was that of isomerism. This was viewed as an error by chemists at first, so little prepared were they to believe that bodies similarly composed could be chemically and physically different. It was in the year 1823 that Liebig announced that his analysis of silver fulminate yielded the same results as Wöhler had found in the preceding year for his silver cyanate. He was confident that his figures were correct, and believed that Wöhler must have made a mistake. A careful repetition of the analyses showed him that both were correct, and so it was proved that two bodies, totally unlike, could and did have the same composition. Gay-Lussac saw that the only explanation of this lay in the different mode in which the elements were combined. In 1826, Berzelius reported on Liebig's fulminate of silver as follows:

"This substance has been made the subject of a new joint investigation by Gay-Lussac and Liebig, and the



result is of the utmost interest. Fulminate of silver dried at  $100^{\circ}$  loses all its water, and in 3 experiments they found between 16.87 and 17.38% cyanogen, the mean being 17.16%. The silver oxide was separated by hydrochloric acid, and was found to be 77.528% of the weight of the salt. These quantities add up to 94.688%. The deficiency is only 5.312%, a quantity absolutely equal to that of the oxygen in the silver oxide. Hence the salt was composed of 77.528% of silver oxide and 22.472% of cyanic acid; but this result is identical with that obtained by Wöhler in his analysis of silver cyanate, in spite of which agreement between the analytical results the two substances have not the same properties. The chief difference is that Wöhler's cyanate of silver, when heated by itself, does not explode, but only burns with moderate intensity; and further, that when decomposed by acids it is completely changed into carbonic acid and ammonia . . . while fulminic acid has explosive properties, and gives ammonia and prussic acid when its salts are decomposed by oxyacids. These facts point unquestionably to a difference in composition." ("Jahresbericht," 1826.)

In 1825, Michael Faraday announced the results of his work on the hydrocarbons from oil-gas, when he demonstrated the existence of butylene, an isomer of ethylene. In 1827, Berzelius commented on this discovery in part as follows:

"The two gases are of like constitution, but . . . a given volume of the one contains twice as many simple atoms as does the other, and this produces a certain dissimilarity in physical and chemical character. . . . Definite knowledge concerning this phenomenon would be of such significance in the doctrine of the composition of vegetable and animal bodies, and would have so important a bearing on organic chemistry, that it must not be accepted as demonstrated until its truth has been subjected to the most severe proof. It is not my intention to dispute the possibility or the actuality of such a fact, but I maintain



that before accepting it with confidence the relation observed by Faraday must be found in a number of other cases."

In 1832 and 1833, Berzelius formally adopted the addition to the doctrine of chemical composition rendered necessary by these observations, and suggested his classical classification of the new phenomena, concluding as follows:

"But since it is requisite that we should be able to express our conceptions by definite and appropriately chosen terms, I have proposed to call substances of the same composition and of different properties 'isomeric,' from the Greek *ισομερής* (composed of equal parts)."

The general designation isomerism has since then been retained. Berzelius soon saw himself necessitated to define more strictly the meaning to be attached to this word and therefore he distinguished between polymerism and metamerism, as special cases of isomerism.

The ideas of Berzelius with regard to the probable cause of isomerism in organic compounds are clearly shown in many of his statements; in his view isomeric compounds are those in which the atoms of the elementary constituents have grouped themselves differently into compound radicals. "The isomerism of compounds in itself presupposes that the positions of the atoms in them must be different." And it appears that he considered it possible to determine the mutual relations of the atoms in their compounds.

and animals were produced by the action of a so-called 'vital force,' and that altho they might be changed into other compounds none of them could be prepared artificially from their elements. Thus, grape-sugar, a compound widely distributed in the vegetable kingdom, by fermentation yielded alcohol, which could be converted into ether, acetic acid, and many other compounds; and all these were considered to be organic, as none of them could be prepared synthetically."

It was Friedrich Wöhler's synthesis of urea which finally removed this obstacle to the growth of organic chemistry. In 1828, Wöhler made the discovery that cyanate of ammonia, which was regarded as an inorganic compound, could be converted into urea, a substance hitherto known only as a product of animal metabolism. This was the first synthesis of an organic compound, and is generally referred to as marking the beginning of scientific organic chemistry. Yet it remained an isolated fact for a long time and failed to shake the belief in a "vital force," a belief which was maintained during the lapse of many years.

In 1830-1831, Liebig perfected and simplified the operations for the ultimate analysis of organic compounds, and this to such a degree that his processes have not required any essential alterations to fit them to modern requirements. These perfected methods enabled Liebig to carry out his famous researches in Giessen, work which renders a brief biographical mention of this master fitting.

Justus Liebig was born at Darmstadt on May 12, 1803. The fact of his father being a dealer in dye-stuffs brought him early into contact with laboratory problems. At fifteen years he was sent to a neighboring town to learn the business of apothecary. But pharmacy was not chemistry, as Liebig was beginning to understand it, so he entered the University of Bonn. Here was certainly change, much "ingenious contemplation," but no chemistry. He traveled to Erlangen, where he heard lectures,

read books, and at nineteen obtained a degree. Then his chance came. His ability being made known to the Grand Duke of Hesse-Darmstadt, he was provided with the means of studying in Paris. There worked those giants, Gay-Lussac, Thénard, Chevreul, Vauquelin, and Dulong; nor was it long before Liebig was received into the laboratory of Gay-Lussac. Liebig had meanwhile won the appreciation of Humboldt; his was a personality that inspired immediate and warm friendships. "Of slender form was he, a friendly earnestness in his regular features, great brown eyes with shady eyebrows which attracted one instantly." It was Humboldt who, in 1824, brought him as extraordinary professor of chemistry to Giessen. Two years later he was elected to the ordinary professorship, which office he held for the next twenty-six years. The dull little town of Giessen became famous; the fires of Liebig's laboratory acted as a beacon light, attracting chastened spirits from the four quarters of the civilized world. For it was not long before the master had roused the Darmstadt Government to build a laboratory where all might come and seek and find. And the movement spread. Liebig, through his pupils, tintured the world; there were other governments than that of Darmstadt, and soon there were other public laboratories than that of Giessen. In 1845 Liebig was created Baron. In 1852 he accepted a call of the Bavarian Government to the Munich professorship of chemistry. Warmly appreciated by the Bavarian court, entering into the social and philosophical life of the university town, courted by all the scientific circles of Europe, yet continually fighting weakening health, Liebig passed the remainder of his life in Munich. He died in 1873.

Liebig devoted his full powers of mind to organic chemistry, but did not neglect inorganic chemistry, as his work on the compounds of silicic acid, alumina and antimony clearly shows. His work in physiological and agricultural chemistry rendered him a general benefactor

of mankind, and, to quote A. W. von Hofmann, "If we sum up in our minds all that Liebig did for the good of mankind, in industries, in agriculture, and in the laws of health, we may confidently assert that no other man of learning, in his course through the world, has ever left a more valuable legacy behind him."

Writing in 1810, Gay-Lussac and Thénard gave, as a reason for the slow progress of animal and vegetable chemistry, the inadequacy of the methods of organic analysis. In their "*Recherches physico-chimiques*," which appeared in 1811, they gave an exhaustive description of a new method of organic analysis, the results of analyses of sugar, starch, gum arabic, milk sugar, wood, and mucic, oxalic, tartaric and acetic acids, as well as of oils, resins and waxes, and the following generalizations made from the results of their work:

1. A vegetable substance is always acid when it contains more oxygen than will form water with the hydrogen.
2. It will be always resinous, oily, or alcoholic when it contains less oxygen than suffices the hydrogen.
3. The body will be neither acid nor resinous, but analogous to sugar or ligneous fiber, when the oxygen and hydrogen are present in just the proportions to form water.

This classification was, of course, of little service, but it was suggestive, and altho no proper classification was possible at this time, the interpretation of Gay-Lussac and Thénard gave a stimulus to the study of the constituents of organic compounds.

Berzelius explained in 1819 that his electrochemical theory could not be extended to organic chemistry, because under the influence of the vital force the elements there possessed entirely different electrochemical properties. In decay, putrefaction, fermentation, etc., he observes phenomena which he regards as demonstrating the tendency of the elements to return to their normal condition. He



in the proof that the so-called "alkarsin," the product of the distillation of acetate of potash with arsenious acid, contained the oxide of an arsenuretted radical  $\text{As}_2\text{C}_2\text{H}_6$  ( $\text{H} = 1$ ,  $\text{C} = 12$ ,  $\text{As} = 75$ ), this radical remaining unchanged in a long series of reactions of that oxide, and being even itself capable of isolation. This "compound element" containing arsenic (an unusual constituent of organic bodies) was thus shown to be a true radical.

Inasmuch as the radical was supposed to be constituted of atoms held together by stronger forces than those which united the group to other atoms, it attained a real significance in the minds of chemists; and as the dualistic theory and the theory of compound radicals became more solidly intrenched in chemistry, they rendered the atomic theory, on which, of course, they were founded, an essentiality, and even after dualism was discredited the only changes were in the ideas as to the nature of the ultimate particles, or atoms.

About this time, however, facts became known which could not be brought into accord with the radical theory, and as a result doubts were expressed as to the theory of dualism; but it was the discovery of the principle of substitution which actually caused this theory to succumb, and paved the way for the so-termed unitary theory.

The conception of equivalence might have led to that of replacement or substitution, since the quantities of two acids were equivalent when they saturated the same quantity of a base. The acid in a neutral salt could thus be replaced by its equivalent without the neutrality being interfered with. The word "replacement" received further justification after Mitscherlich had studied the phenomena of isomorphism. It could then be said that certain elements in a crystal might be replaced by others without alteration of the crystalline form. Such substitutions possessed the peculiarity, however, that they were not connected with any proportions by weight, and it may thus appear all the more remarkable that they should

render important assistance in the determination of atomic weights. The hypothesis underlying the phenomena of isomorphism was that one atom could only be replaced by one other; that is to say, that the numbers of the atoms in isomorphous compounds must be identical. Since chemically similar substances had alone been compared, an extension of the prevailing views, based on the phenomena of isomorphism, would have been quite possible; but this class of phenomena had never led to any attack upon the system.

In the bleaching of wax by means of chlorine, Gay-Lussac had observed that for every volume of hydrogen eliminated, an equal volume of chlorine was taken up. He had also found the same thing in the action of chlorine on hydrocyanic acid. In the course of their investigation of the benzoyl compounds, previously referred to, Wöhler and Liebig, when acting with chlorine upon bitter almond oil, had discovered benzoyl chloride; and they expressly remark that this substance is produced from the bitter-almond oil by two atoms of chlorine taking the place of two of hydrogen.

In the year 1834 Dumas, à propos of an investigation on the mutual action between chlorine and oil of turpentine, but more especially of his work upon the production of chloral from alcohol, condensed into two empirical rules the facts with regard to substitution, for which he proposed the designation *metalepsy* (*i.e.*, exchange, *μετάληψις*). These were not intended to comprize a theory of substitution, as his first utterances on the subject show, but only to give expression to the facts. They were as follows:

"When a compound containing hydrogen is exposed to the dehydrogenizing action of chlorine, bromine, or iodine, it takes up an equal volume of chlorine, bromine, etc., for each atom of hydrogen that it loses.

"If the compound contains water, it loses the hydrogen of this without replacement."



The second of these rules was deduced from the transformation of alcohol into chloral, and was thus intended to explain the mode of formation of the latter and at the same time to support Dumas' view of the constitution of alcohol, the latter being regarded by him as a compound of ethylene and water.

By means of various examples, Dumas further endeavored to prove the general validity of the laws which he advanced. In establishing the correct composition of the Dutch oil he pointed out that the chloride of carbon obtained from it by means of chlorine, and examined by Faraday, supplied a new argument in favor of the accuracy of his views. He also found similar support in the action of chlorine on hydrocyanic acid, on bitter almond oil, etc.

However, he was unsatisfied with this, and extended his statement to one of greater significance, regarding oxidations as cases of substitution, as, for instance, the conversion of alcohol into acetic acid.

While Dumas limited himself at this time (1835) to condensing the known facts into the above laws, Auguste Laurent (1807-1853), a pupil of Dumas, went further, and considered the nature of the compounds resulting from substitution and made a comparison of them with the original ones. He was thereby induced to enunciate the proposition that the structure and chemical nature of organic compounds are not materially changed by the entrance of chlorine and the separation of hydrogen. This law is the core of the substitution theory proper, of which Laurent was the propounder.

Laurent endeavored to give expression to the observed facts, and to the hypotheses based upon them, in the so-called nucleus theory. This theory is of importance in the science (altho it never obtained any general recognition in it) because chemists have adopted, if in another form, many of the ideas embraced by it, and also because it was adopted by Gmelin as the basis of the organic portion of

his excellent handbook. On this account the chief points of Laurent's doctrines will be stated.

According to Laurent, all organic substances contain certain nuclei, which he calls either fundamental ("radicaux fondamentaux") or derived. The former are compounds of carbon with hydrogen, in which the mutual proportion of the number of the atoms is a simple one (1 to 2, 3, 4, etc., 2 to 3, etc.). For any definite proportion, several nuclei exist which are polymeric among themselves. Besides, these fundamental radicals are so chosen that the hydrogen and carbon atoms contained in them occur in pairs.

The derived nuclei ("radicaux dérivés") were produced from the original nuclei, either through the substitution of hydrogen by other elements or by the addition of other atoms.

This theory manifestly sprang from the old radical theory, but with an important change, namely: the radical here is not an unchanging group of atoms, but it is a combination which can be changed through the substitution of equivalents. It is but a step in the evolution of the modern theory, as seen in the benzene nucleus.

The nucleus theory was regarded as unscientific by Liebig, and Berzelius opposed it, but the latter was moved before long by Malaguti's investigation of the simple and compound ethers—in which he demonstrated that the chlorine atoms again played the part just as the hydrogen atoms they had displaced—and, as Armitage observes in his "History of Chemistry," he "saw that here was the thin edge of a most potent wedge, which, unless immediately removed, might break down the whole fabric of that chemical theory he had spent so much on building."

Before Laurent, in conjunction with Gerhardt, had again brought forward his ideas in a more perfect form, Dumas entered the lists to do battle against the radical theory, and, with this, against the dualistic idea in general. His beautiful discovery of "chloracetic acid" afforded him

the immediate occasion for this, and he now gave in his adhesion to Laurent's opinions, which formerly he would have nothing to do with.

By the action of chlorine, in sunlight, upon acetic acid, Dumas had obtained a crystalline substance whose composition could be expressed by the formula  $C_2Cl_2H_2O_2$ , and which could, therefore, be regarded as acetic acid,  $C_2H_4O_2$ , in which six atoms or volumes of hydrogen were replaced by six atoms of chlorine. The interesting and important part of this reaction lay in the properties of the new compound, which Dumas called chloracetic acid. This acid had the same saturating capacity as acetic acid, so that Dumas was able to assert that by the entrance of chlorine in place of the hydrogen, the chief character of the compound was not altered; or, as he expresses himself, "that in organic chemistry there are certain types which persist even when an equal volume of chlorine, bromine, or iodine is introduced into them in place of the hydrogen which they contain."

He was thus led to the same view which had already been taken up by Laurent, but his theory of types (1839) was hardly a mere application of the views of Laurent. The principal propositions of this theory were as follows:

1. The elements of a compound body can, in many cases, be replaced by equivalents of other elements or of compound bodies which play the part of simple ones.

2. If such a substitution occurs equivalent for equivalent, the compound in which the replacement has taken place retains its "chemical type," and the element or group which has been taken up plays in it the same part as the element which has gone out.

The term "chemical type" failed to satisfy Dumas, however, and he permitted it to merge into that of "mechanical type," which included all compounds which might be supposed to be formed from one another by substitution, even tho they differed in properties.

Berzelius could not accept these views, and when Dumas

characterized his electrochemical theory as erroneous, an embittered discussion ensued which lasted for years. The proposition of Dumas that every chemical compound forms a complete whole and cannot therefore consist of two parts, that its chemical character is dependent primarily upon the arrangement and number of the atoms, and in a lesser degree upon their chemical nature, proclaimed a decided unitarism, and was therefore violently opposed by Berzelius.

Berzelius sought to get over the difficulties which the substitution of hydrogen by chlorine and other elements involved, by arguing that compounds formed in this manner must have a constitution different from that of the original ones. But here he entered upon dangerous ground, and was thereby led, prudent investigator as he was, into the most utter contradictions of the principles which he had formerly held to be inviolable.

Facts now increased which went to demonstrate the correctness of the theory of substitution, and in 1842 Mellens found that by the action of potassium amalgam on a water solution of trichloroacetic acid, its chlorine was completely replaced by hydrogen, acetic acid being reproduced. This was a discovery of the greatest import, as it showed inverse substitution was possible, yet it did not shake Berzelius's faith. He merely decided to look upon acetic acid in the same way as its chlorine derivative—i.e., as a copulated oxalic acid with the copula methyl,  $C_2H_5$ , formulating the two compounds thus:



This was practically giving up the fight, as by it he acknowledged that the "Paarling," or copula, could undergo substitution, and that its exact nature did not have a predominating influence in determining the nature of the compound into which it entered. Yet Berzelius remained

an opponent of the theory of types until his death in 1848, and his adherents experienced great difficulty in reconstructing radicals anew from his copulæ after his death.

In 1845, A. W. Hofmann discovered the substituted anilines, and observed that it appeared without doubt that chlorine or bromine could assume the rôle of hydrogen in organic compounds, taking their electro-negative character with them into the new compounds. Liebig commented on Hofmann's report as follows: "The author appears to have definitely proved that the chemical nature of a compound does not in any way depend upon the nature of the elements contained in it as is assumed by the electro-chemical theory, but entirely on their arrangement." Liebig now turned to the unitary theory and opposed Berzelius's attempted explanations. Other prominent chemists, too, became his opponents, and yet, in spite of the slight regard in which the radical theory was held in many quarters, it soon became evident that, for the investigation of chemical constitution, the assumption of radicals, which had been displaced by the theory of types, was indispensable.

In the fifth decade a fusion of the radical theory with the doctrine of types occurred on the Unitary side, and as a result of the work of Auguste Laurent and Charles Gerhardt (1816-1856) the older theory of types was transformed into the new theory.

In 1839, Gerhardt published his views on the process which occurs when an element is replaced by a group of atoms. In his opinion it was not a substitution, but a union of two residues to a unitary whole and not an articulated binary compound. He termed these groups of atoms "*le reste*" or "*le restant*," and later developed his theory of residues, according to which a residue could have the composition of a compound radical but was not present as such in a compound. His conception of radicals soon replaced the older views, and its introduction into the theory of types induced a fusion of both theories.

The first advance in this direction was made in 1849, when C. A. Wurtz (1817-1884) discovered the compound ammonias. Hofmann found another method of preparing the bases discovered by Wurtz, and the "typical" view of these bases was first arrived at by means of his investigations. He showed that in the amine bases, as well as in aniline, the two hydrogen atoms of the amide could be replaced by alcohol radicals. A. W. Williamson (1824-1904) then demonstrated that in a similar manner the alcohols and their ethers could be referred to the type water. He also pointed out that acetic acid must have a constitution similar to that of alcohol, and proposed to call the radical  $C_2H_5O$ , obtained from ethyl by oxygen substitution, ethyl. Gerhardt, employing a reaction similar to that by which Williamson had prepared the ethers, discovered the anhydrous acids; and chemists began to attempt to find among the more simple inorganic compounds other types for organic compounds, thereby giving rise to Gerhardt's theory of types. According to this theory, the organic compounds of known constitution can be classified under four types, namely, hydrogen, hydrochloric acid, water, and ammonia; for example, the hydrocarbons, aldehydes, and the acetones or ketones were classed in the first type; the halides (chlorides, bromides, iodides, and fluorides) in the second; the alcohols, ethers, monobasic acids, and sulphides and hydrosulphides in the third; and the amines were placed in the fourth type.

The general arrangement and the comprehensive character of Gerhardt's system leave nothing to be desired. Even altho views have been considerably changed and cleared up since that time, and altho one is compelled, from the modern standpoint, to look upon the types as insufficient, still Gerhardt's services to chemistry can never be questioned. Unfortunately he did not live to witness the reception which was extended by many chemists to the views laid down by him in the fourth volume of his "*Lehrbuch der Organischen Chemie*." The type theory was



particularly extended by the assumption of "mixed types," which was intended to render clear the relations of many organic compounds to two or more types. This was particularly applied by August Kekulé.

It was also in the fifth decade that Hermann Kolbe (1818-1884) revived the much-ridiculed copulæ. He and Sir Edward Frankland (1825-1899) were followers of Berzelius, and held similar views to Gerhardt, but as they did not accept at that time either the new atomic weights or the existence of radicals containing oxygen, they made use of other formulæ.

Kolbe united the conclusions deduced from his researches with the declining theory of Berzelius; he infused the latter with new life by casting aside whatever of it was dead and replacing this by vigorous principles. From his own and other investigations he came to the conclusion that the unalterability of radicals, as taught by Berzelius, could no longer be maintained, since the facts of substitution had to be taken into account. He did, indeed, adopt Berzelius' hypothesis of copulæ, but attached another meaning to these, since he allowed that they exercised a not inconsiderable influence upon the compounds with which they were copulated.

He endeavored to make this theory have a deeper bearing upon the constitution of organic compounds, and, as a result of the influence of several important researches, his ideas regarding copulæ and conjugated compounds were altered several times. His theoretical views and, with them, the revived radical theory reached their completed form in a contribution published in 1859.

The principal result of Kolbe's speculations is given as follows: "Organic compounds are all derivatives of inorganic, or result from the latter—in some cases directly—by wonderfully simple substitution-processes." This idea runs through the 1859 contribution and is illustrated by numerous examples from the wide field of organic chemistry.



## CHAPTER XIII

### VALENCE, THE CONSTITUTION OF ORGANIC COMPOUNDS, AND THE DEVELOPMENT OF STEREO-CHEMISTRY

IN the preceding chapter mention has been made of the influence exerted by Frankland on the views developed by Kolbe respecting the constitution of organic compounds. It was Frankland who, in his now classical paper—"A New Series of Organic Compounds containing Metals"—demonstrated that the pairing of the radicals with the elements was to be explained on the ground of some characteristic property of the atoms, and thus he expelled the useless part of the radical theory (1852).

Frankland observed that "When the formulæ of inorganic chemical compounds are considered, even a superficial observer is struck with the general symmetry of their constitution; the compounds of nitrogen, phosphorus, antimony and arsenic especially exhibit the tendency of these elements to form compounds containing 3 or 5 equivalents of other elements, and it is in these proportions that their affinities are best satisfied; thus in the ternal group we have  $\text{NO}_3$ ,  $\text{NH}_3$ ,  $\text{NI}_3$ ,  $\text{NS}_3$ ,  $\text{PO}_3$ ,  $\text{PH}_3$ ,  $\text{PCl}_3$ ,  $\text{SbO}_3$ ,  $\text{SbH}_3$ ,  $\text{SbCl}_3$ ,  $\text{AsO}_3$ ,  $\text{AsH}_3$ ,  $\text{AsCl}_3$ , etc.; and in the five atom group  $\text{NO}_5$ ,  $\text{NH}_5$ ,  $\text{NI}_5$ ,  $\text{PO}_5$ ,  $\text{PH}_5$ , etc. Without offering any hypothesis regarding the cause of this symmetrical grouping of atoms, it is sufficiently evident, from the examples just given, that such a tendency or law prevails, and that, no matter what the character of the uniting atoms may be, the combining power of the attracting element, if I may be

allowed the term, is always satisfied by the same number of these atoms."

He then proceeded to represent the organo-metallic compounds obtained by formulæ which brought out the analogy with the inorganic types, from which they were thought to have been derived.

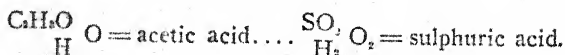
From his work on the organo-metallic compounds, Frankland developed the doctrine of the valence of the elements, the germ of which may be recognized in much that has gone before, particularly in the law of multiple proportions, which stated that the elements show different yet definite stages in their combinations.

The so-called doctrine of the polybasic acids contributed materially to the development of ideas upon the subject of the saturation capacity of the atoms. Gay-Lussac, Gmelin, and others inclined to the assumption that the atoms of the various metallic oxides contained one atom of oxygen united to one atom of metal, and that these oxides combined with one atom of acid to form neutral salts. Berzelius also, after 1826, considered that this combining proportion was the rule. However, by Thomas Graham's famous investigation of the phosphoric acids (1833), it was shown that a view so simple as this, according to which almost every acid was looked upon as monobasic, was untenable. Graham proved that in the ortho-, pyro-, and meta-phosphoric acids, for each "atom" of phosphorus pentoxide there were three, two and one "atoms" of "basic water," these latter being replaced by equivalent amounts of metallic oxides.

The saturation capacities of these acids were in this way shown to be dependent upon the amounts of "basic water" which entered into their constitution. Liebig extended this to many other acids and distinguished between mono-, di-, and tri-basic acids, and the property was referred to as the "basicity" of the atoms, a term which, with the ideas inherent in it, clung for some time to the theory of valence. In 1857, for example, the terms "basic-

ity," "valency," and "atomicity" were used as synonymous, and as the measure of the number of hydrogen atoms that could be replaced or held in combination.

The idea of "basicity" was soon extended to the compound organic radicals. In 1855, C. A. Wurtz (1817-1884), a pupil of Liebig and Dumas, showed that glycerine ( $C_3H_8O_3$ ) may be regarded as the hydrate of the radical  $C_3H_5$ . Four years previous A. W. Williamson (1824-1904) had expressed the view that a large number of compounds may be referred to the type of water, the monobasic acids to one molecule, and the polybasic acids, which are of greater molecular complexity, to a condensed water type. He wrote



Wurtz now showed that the composition of glycerine could be represented by the formula



$O_3$ , which was similar to the formula by which,  $H_3$

in accordance with the ideas of Williamson, ordinary  $(PO)'''$

phosphoric acid  $O_3$  was represented.  $H_3$

Gerhardt in his "Traité de Chimie Organique" stated that "In order to compare the radicles among themselves, I propose to refer them all to the radicle of hydrogen, and consequently I name them monatomic, diatomic, triatomic according to the quantity of hydrogen which they are capable of replacing in the type  $H_2O$ —i.e., according to whether they are equivalent to 1, 2, or 3 atoms of hydrogen—so for instance in alcohol and in ether:



$\text{C}_2\text{H}_5$ , the radicle ethyl, is monatomic because it replaces H (one atom of hydrogen) in the type water."

The terms "monatomic" and "polyatomic" had been employed much earlier, but in a different sense. Thus, in 1827, Berzelius called fluorine, chlorine, etc., "polyatomic," because several atoms of these halogens unite with a single atom of another element. In 1833, Gaudin de Saintes used the same terms to express the number of atoms in a molecule, in which sense they were used by Gmelin, Clausius, and Odling. Williamson attached the idea of capacity for saturation or atomicity of the radical to the number of hydrogen atoms capable of substitution, and the notion of atomicity was soon extended to the known compound radicals and played an important part in the theories of types, etc., which obtained in organic chemistry.

Frankland's speculations concerning the substitution value of radicals compared with that of elementary atoms were of great importance, yet they did not meet with immediate approval.

By 1858, however, the valence theory had made rapid progress. In this year August Kekulé first deduced the valence of carbon from its simplest compounds, declaring it to be tetravalent. This had already been recognised by Kolbe and Frankland, if not expressly stated by them. But Kekulé rendered further and much greater service by inquiring into the manner in which two or more of these tetravalent carbons were united with one another. The doctrine of atomic chains, open and closed, sprang from this, and the domination of the structural idea in chemistry became complete.

In the same year and independently of Kekulé, M. S.

Couper arrived at conclusions almost identical with those of Kekulé.

Both Kekulé and Couper expressed with absolute definiteness the axiom that the "atomicity of the elements" was to be made use of for arriving at the constitution of chemical compounds. The idea of the term "atomicity" had without any doubt been introduced by Frankland six years previous to this. The further development of the above axiom and its utilization in the theory of the linking of atoms was carried out mainly by Kekulé, and in the succeeding years also by Butlerow and Erlenmeyer.

While the radical and type theories were attempts at securing an idea of the structure of chemical compounds, it was the valence theory which rendered it possible to furnish a lucid answer to the question as to the composition of such bodies; and, especially after the year 1870, the determination of the constitution of complex molecules became the higher aim of chemistry.

Some rudiments of systematic classification had before this been introduced into organic chemistry, and these classificatory beginnings were of great assistance in the erection of structural chemistry. In 1836, Laurent, when he brought forward his nucleus series, arranged organic compounds in series, and it was in 1841 that Gerhardt entered on a research to discover some general law which might suggest an all-sufficing system of classification, and the following year he was ready with his "ladder of combustion"—with its highest rung cerebral matter, its lowest carbonic acid, water and ammonia—to enfold the whole science of organic chemistry. He soon found, however, that this arrangement, according to mere complexity of composition, was no sufficient classification, so he betook himself to another line of inquiry. A note of triumph seems to ring through the following lines from the preface to his "*Précis de Chimie Organique*," published in 1844: "I have succeeded in establishing homologous series.

. . . These have indicated to me the means of classifying organic substances in natural families, and of disposing them on a kind of combustion ladder." As a matter of fact, it was only the word "homology" that Gerhardt could claim as his own. Two years earlier J. Schiel had shown that a very simple relation existed between the alcohols then known, that their radicals might all be represented by the general expression  $nR + H$ ,  $R$  suggesting the group  $C_2H_5(C=6)$ ; moreover, in the same year Dumas had demonstrated the existence of a similar relation between the several members of the fatty acids known to him. Yet Gerhardt generalized from this fact of homology and proved the possibility of predicting the existence of terms unknown in his series.

Many systems of classification were suggested during the sixth decade, the classification by series as that of Schiel and Dumas, that of series depending upon formulæ, series depending upon chemical behavior, and many other systems. The lack of agreement among chemists, however, as to the formulæ belonging to the different compounds, as to the relative weights of the molecules, the atomic weights, and even the number of atoms, prevented a general acceptance of any of the classifications proposed until Kekulé established the fact of the tetravalence of the carbon atom, showed the difference between saturated and unsaturated compounds, and deduced his chain formulæ.

About 1860 Frankland's views regarding a saturation capacity peculiar to the elements were accepted either deliquescently or expressly by most chemists, but it was considered that this saturation capacity, under certain circumstances, might be a varying one. In 1856, Gerhardt had stated that nitrogen was sometimes triatomic and sometimes pentatomic. This view was also held by Frankland, Wurtz, Williamson and Couper, and the latter three considered that the valence was also variable in the cases of many other elements. Kolbe thought that it must be



assumed that a constant valency was characteristic of a few elements and a varying one characteristic of many more, since he perceived in it another expression for the law of multiple proportions and nothing was known concerning the cause of valence. As early as 1854, Kolbe had concluded that each element possessed a maximum saturation capacity, but that lower stages of saturation might exist along with this; and toward the beginning of the sixties, several chemists who took an active part in developing the structure theory expressed the same opinion in a more definite manner. Erlenmeyer, in particular, maintained in various papers, and afterward in his "Lehrbuch der organischen Chemie," that each element possesses a maximum valency, or that each is furnished with a definite number of "Affivalenten" or affinity-points ("Affinitätspunkten"), only part of these, however, being in many cases combined with the affinity-points of other elements.

Kekulé's theory of the constant valence of the elements could not withstand the critical examinations to which it was subjected, however, and in the course of the last forty years the majority of chemists have adopted the view that the atoms of most of the elements possess a varying saturation capacity, varying according to the conditions.

Altho the structure theory was unable to accomplish the extreme expectations which aimed at a knowledge of the spacial arrangement of the atoms, it possessed none the less great practical value. The development of organic chemistry since the middle of the sixth decade shows in fact that, through the aid of the structural hypothesis, the discovery of new modes of formation and decomposition of compounds, the recognition of the relations existing between various classes of bodies, and, especially, the interpretation of the constitution of numerous organic substances became possible. Kekulé's theory of the aro-

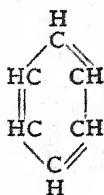


matic compounds forms the most striking proof of this.

In 1865-1866, taking the quadrivalence of carbon as his principle, Kekulé called attention to the fact that in the fatty compounds the carbon atoms are linked together by one valence of each. In the case of benzene, the next simplest assumption was made, in accordance with which the carbon atoms are linked together by one and two valencies alternately, so as to form a closed chain or ring. Of the twenty-four affinities of the six carbon atoms, eighteen are employed in linking carbon to carbon, thus:

$$\begin{array}{r} 6 \qquad 6 \\ - .4 + - .2 = 18 \\ 2 \qquad 2 \end{array}$$

Six valencies then remain which are satisfied by the six hydrogen atoms of the benzene. Hence, according to Kekulé, benzene may be represented by means of a regular hexagon whose sides are composed of single and of double lines alternately, the CH groups occupying the corners, thus:



Kekulé and his pupils, together with many other chemists who had busied themselves with the derivatives of benzene after this view had been published, now directed their efforts to comparing all the known and rapidly increasing observations bearing upon this class of bodies with the deductions drawn from the above formula, and therewith to proving by actual experiment the admissibil-

ity of the assumptions on which the formula was based. The result was that Kekulé's anticipations were realized and his hypothesis substantiated.

In 1866, Kekulé had stated that "What is wanted is that the largest possible number of substitution products of benzene should be prepared by the most diverse methods; that they should be most carefully compared with regard to isomerism; that the modifications so found should be counted. . . ."

And in the 1867 edition of his text-book, he called attention to a number of cases of isomerism which at that time had received no explanation. Among these we find that of ethylene chloride with ethylidene chloride; of acetal with diethyl glycol; for maleic and fumaric, for mucic and saccharic acids, the last effort of his philosophy had only found him the two formulæ  $\begin{matrix} C_4H_2''O_2 \\ H_2 \end{matrix} \left\{ \begin{matrix} O_2 \\ \end{matrix} \right.$  and  $\begin{matrix} C_4H_2''O_2 \\ H_2 \end{matrix} \left\{ \begin{matrix} O_2 \\ \end{matrix} \right.$  respectively. Kekulé instanced, too, those bodies which only differed in their effect on polarized light, the tartaric, the malic and camphoric acids, and the amyl alcohols.

It was owing to these cases of isomerism that structural formulæ could not be assigned. In some cases a greater number of isomeric bodies were known than could possibly be accounted for by any arrangement of the atoms in formulæ upon a plane surface, retaining, of course, the accepted views as to valence, etc., and since these isomers differed principally in certain physical properties, they were at first termed "physical isomers." The study of these resulted in the consideration of the arrangement of atoms in space—the chemistry of space, or Stereochemistry, in which branch of the science an extended view of atomic grouping was essayed.

Modern stereochemistry was anticipated by Emmanuel Swedenborg in 1721, when he made an attempt to explain the phenomena of chemistry and physics on geo-

metrical principles in his 'Prodromus Principiorum rerum Naturalium sive Novorum Tentaminum Chymiam et Physicam Experimentalem Geometrice Explicandi,' and similar beginnings were made by Johann Barchusen ten years earlier.

In 1864 Carius, who first used the term "physical isomerism," explained it as follows:

"I have tentatively expressed a view as to the cause of what I call 'physical isomerism.' Substances [which exhibit this property] yield, under the same or nearly the same conditions, products which are either identical or physically isomeric. According to our present views, I think it improbable that such substances should have their atoms differently arranged—*i.e.*, that they should be metameric. But it is quite conceivable that in the formation of physical isomers differences of condition may cause the production of substances with the same arrangement of the atoms within the molecule, but with a different aggregation of these molecules; and that thereon depends the difference in their properties. . . . Thus we must consider as certainly only physically isomeric a large number of the substances distinguished by the difference of their action on polarized light, such as the two modifications of amyl alcohol, the tartaric acids, the malic acids, etc."

This explanation was inadequate, and in 1873 Johannes Wislicenus (1835-1902), who succeeded Kolbe as professor of chemistry at Leipzig in 1885, suggested the substitution of the term "geometrical isomerism" for "physical isomerism." He had been engaged in an investigation of the various modifications of lactic acid, and had found that the ethylene lactic acid, or hydracrylic acid, prepared by Beilstein by treating  $\beta$ -iodo-propionic acid with silver oxide, possessed properties different from those of the ethylene lactic acid obtained from ethylene cyanhydrin. This difference was so marked that he thought it might be explained by assigning the two acids different structural

formulae. The first was optically inactive, while the second (paralactic acid) was dextro-rotary. This one point of difference appeared hardly sufficient to "make it necessary to assign to paralactic acid a structural formula other than that of the fermentation lactic acid." It seemed much more likely that here, at any rate, were cases of what Carius had called "physical," but what Wislicenus now proposed to call "geometrical isomerism." He said, "My conclusion for the present is to declare paralactic acid and the fermentation lactic acid as most probably only geometrically isomeric. Their great similarity, even identity in all chemical properties, the ease of transformation, on heating, of the first into the second, and their differences, particularly in optical behavior, may all alike be explained on this basis.

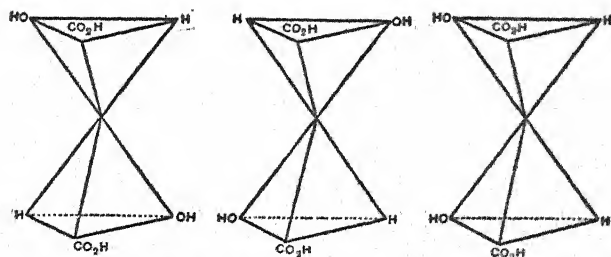
"Concerning the special 'how' of this explanation, I am engaged in experimental investigations."

The next year J. H. Van't Hoff furnished an answer to this. However, before giving his exposition, mention must be made of Louis Pasteur's (1822-1895) pioneer work in this field. Pasteur studied the various tartrates crystallographically, and showed that there are four isomeric tartaric acids, viz.: racemic acid, inactive tartaric acid, and right and left rotating tartaric acids. He showed, moreover, that the two latter acids crystallize in similar, but in oppositely built-up (enantiomorph) forms; that they both rotate a ray of polarized light through equal angles, but in opposite senses; and that when mixed in equal quantities they yield optically inactive racemic acid. Further, he succeeded in decomposing racemic acid again into the two optically active tartaric acids by three different methods.

Pasteur established the correlation of molecular dissymmetry and rotary power in these investigations, and it remained to discover under what conditions the dissymmetry could obtain in two molecules structurally identical. This was undertaken in 1874 by J. H. Van't Hoff in Hol-

land and J. A. Le Bel in France, who in papers published that year offered an explanation practically the same for cases of isomerism which could not be included under the theories of the time.

Van't Hoff states that in general Le Bel's original paper and his were in accord, but that while Pasteur's researches formed Le Bel's starting point, he took for his own "Kekulé's law of the tetravalence of carbon, [to which he]



TARTARIC ACIDS. III., meso-tartaric acid.  
I., active acid. II., other active acid. (Inactive, divisible.)  
IV., racemic acid.  
(Inactive, indivisible.)

added the hypothesis that the four valencies are directed toward the corners of the tetrahedron in the center of which is the carbon atom." To quote from Freund's 'Study of Chemical Composition,' "Van't Hoff introduced no fundamental change in, or addition to, the original valency hypothesis; a two-dimensional representation of molecular structure could not at any time have been considered as really true to the actual occurrence, but it was legitimate to use it, because of its greater simplicity, as long as it proved adequate to the purpose. And with this recognition and restriction we continue to use plane structural formulæ in the majority of cases." Van't Hoff, following up the suggestion that may be found implied in Pasteur's paper, and that was explicitly stated by Wisli-

cenus, introduces into the science the consideration of the arrangement of atoms in space:

"Stereochemistry [from στερεός, solid], in the restricted sense of the word, comprizes chemical phenomena which demand a consideration of the grouping of atoms in space."

Carbon compounds only were considered at first, but the scope of the phenomena dealt with has been extended and now includes compounds of trivalent and pentavalent nitrogen, of tin, and of sulphur.

Van't Hoff's theory of the asymmetric carbon atom, however, met with difficulties on its enunciation. To quote from F. P. Armitage's "History of Chemistry":

"When Van't Hoff enunciated his theory of the asymmetric carbon atom, he was able to say, with much show of truth, that all optically active substances did contain certainly one such atom. Soon, however, were heard dissentient voices. What of propyl alcohol, asked one; and of styrolene, demanded another. The propyl alcohol owes its activity to traces of amyl alcohol, answered Henniger; the styrolene is impure, said Van't Hoff; and their evidence was irrefutable. But Van't Hoff could not, in 1874, maintain that the presence of one asymmetric carbon atom necessarily implied optical activity; for secondary amyl alcohol and its derivatives, also propylene alcohol, were certainly inactive, yet all contained an asymmetric carbon atom. The problem set the stereochemists was somewhat similar to that of the relation between tartaric and racemic acid, so happily solved years before by Pasteur. His methods were recalled; and Le Bel soon showed that these inactive bodies were in reality mixtures of two optically opposite isomers, and, others helping, that indeed every substance with but one asymmetric carbon atom was equally capable of 'mesotomism.' The four varieties of tartaric acid had offered no difficulty; with two asymmetric carbon atoms similarly habited there was necessarily neutralization or duplication of optical activity.



But where two or more carbon atoms occurred, asymmetric by union with different radicals, as in the sugars and their derivatives, many more cases of physical isomerism suggested themselves, and have since been verified. Without doubt the asymmetric carbon atom has made a triumphant progress, winning for Le Bel the Jecker prize of 1881, for Van't Hoff a dominant voice in the scientific councils of the world; it will rank with the phlogiston of Stahl, the oxygen of Lavoisier, the atom of Dalton, and the dualism of Berzelius."

Among the most noted workers in the field of stereochemistry have been A. von Baeyer, Wallach, Victor Meyer, Riecke, Bischoff, Werner, Hantzsch, Auwers and Overton. Even now the subject is in its infancy, and stereochemical theories are as yet insufficiently advanced to present a clear view of the question of geometrical isomerism, yet, as Ladenburg has said, "It is beyond doubt that the founding and development of stereochemistry (a name which originated with Victor Meyer) is the most important thing that was accomplished in organic chemistry during the last two decades of the nineteenth century. Stereochemistry possesses a significance for this period similar to that which the foundation and introduction of the theory of aromatic compounds possessed for the twenty years preceding."



## CHAPTER XIV

### PROGRESS IN INORGANIC CHEMISTRY DURING THE MODERN PERIOD

A RAPID growth in inorganic chemistry ensued after the introduction of the New Chemistry by Lavoisier. A mass of information concerning the nature of the elements and their compounds was accumulated, and many new bodies were discovered. However, even now, after the accurate study of the chemical behavior of mineral substances by many careful investigators, we are still far from a definite knowledge of the nature of all the elements and their compounds, and new bodies are from time to time added to the extensive series already known. In the case of the elements, for example, Lavoisier in his 'Traité de Chimie' mentioned twenty-six, while eighty-one are at the present time accepted. An endeavor to sketch the important advances in inorganic chemistry since the time of Davy and Gay-Lussac will be made in this chapter.

Cadmium was discovered by Stromeyer in 1817 and about the same time by Hermann. It was named by Stromeyer "cadmia fornicum" (furnace zinc), because it was found in the zinc furnace, cadmia being the original name for zinc.

In the same year lithium was discovered by Arfvedson in petalite and spodumene. The metal was first obtained by Bunsen and Matthiessen in 1855. The name is Greek and means stony, and the metal was so called because it was then supposed to be found only in rocks, and not in the plant and animal bodies.

Silicon was first isolated in 1810 by Berzelius by fusing together iron, carbon and quartz, and Wöhler showed that it exists in the crystalline form as well as in the amorphous state.

In 1827, Wöhler isolated aluminium by the action of potassium upon its chloride, and eighteen years later St. Claire Deville prepared the metal on a large scale by using sodium, while Bunsen effected its preparation by electrolytic means. Aluminium is now prepared in quantity by the electrolytic decomposition of the oxide, alumina, dissolved in cryolite. Beryllium, or glucinum, was also obtained by Wöhler, who effected its isolation in 1828 by the action of potassium upon the chloride. Bromine was isolated by Balard in 1826 from the mother liquor of sea-salt, and was further investigated three years later by Löwig; along with iodine, which was discovered by Courtois in 1811 in the ashes of sea plants, and chlorine, it constituted the group of halogen elements of Berzelius, since fluorine was then unknown. The latter was first isolated in 1886 by Moissan by the electrolysis of hydrogen fluoride in the presence of potassium fluoride.

Tellurium, which had been discovered by Müller von Reichenstein in 1782, was thoroly investigated by Berzelius, who discovered an element chemically analogous to it—selenium—in 1817.

The isolation of the metals comprising the cerium and yttrium groups has presented numerous difficulties. Altho the discovery of yttria—impure, it is true, from admixture with other earths—was accomplished by Gadolin in 1794, and investigators have busied themselves with the question, the chemistry of the cerium metals is not even yet completely elucidated, and may possibly remain unsolved for a considerable time to come. After Klaproth and Berzelius had independently prepared cerium sesquioxide from cerite, and the latter had identified this as the oxide of a metal, Mosander discovered two new oxides in crude yttria, the metals of which—lanthanum (1834)

and didymium (1841)—he isolated. Two years later (1843) he added to these two others, erbium and terbium, whose existence and nature is not yet, however, definitely settled, in spite of the admirable work which has been done on the subject. This has given us a better knowledge of yttrium, while yttria, which was formerly held to be a homogeneous substance, has proved itself a mixture of the oxides of various metals, of which, however, only one or two have as yet been isolated; for example, the discovery of scandium by Nilson and Cleve in 1879, and of ytterbium by Marignac. The most recent additions to the knowledge of chemistry of this group of elements and their compounds have been made by Welsbach, Drossbach, Krüss, Winkler, Crookes, Brauner, Baskerville, Urbain and others. Welsbach separated didymium into praseo- and neodmium. An analytical method has been elaborated for the separation of the various constituents of the cerium, ytterbium and thorium earths, which has been of help in the manufacture of mantles for incandescent light burners. Quite recently Urbain has separated ytterbium into two other elements—neoytterbium and lutecium. In spectrum analysis, chemistry now possesses an exceedingly valuable instrument for investigating rare metals and earths, and its use in the last five decades has been extensive.

Spectrum analysis has grown out of some apparently insignificant and disconnected observations made by Marggraf, Scheele, Herschel and others upon the light emitted by flames colored by certain salts. The spectra of such flames were investigated by various scientists, among whom Talbot, Miller, Alter and Swan deserve first mention; but it was only after Kirchhoff (in 1860) proved the definite statement—that every glowing vapor emits rays of the same degree of refrangibility that it absorbs—that spectrum analysis became developed by Bunsen and himself into one of the great branches of our science.

Its importance for analytical chemistry, especially in the discovery of new elements, is almost beyond mention, and it opened up a new era in chemistry.

Roscoe once said, "The spectroscope, next to the balance, is the most useful and important instrument which the chemist possesses." Crookes has remarked, "If I name the spectroscope as the most important scientific invention of the latter half of this century, I shall not fear to be accused of exaggeration." The very importance of the subject prevents an entrance into any long discussion of it here. It has come to form a distinct branch of chemical science. In the hands of men like Bunsen and Crookes it has explored the recesses of the rocks for minute traces of hidden treasures, while with it workers like Miller, Huggins and Lockyer have fathomed the abysses of space and determined the constitution of the stars.

Among the elements discovered by the use of the spectroscope were rubidium and cesium in lepidolite and in the Durkheim mineral water by Bunsen and Kirchhoff; indium by Reich and Richter, in 1863, as a constituent of Freiberg zinc blende; gallium in 1875 by Lecoq de Boisbaudran; and thallium by Crookes in 1861. The chemical nature of the last-mentioned metal was established by Lamy in the same year.

The knowledge of the metals discovered in the preceding era was greatly enlarged by investigations conducted during this period. The analogues of nitrogen—phosphorus, arsenic, antimony and bismuth—were carefully examined, and the atomic weight which Berzelius determined for phosphorus was confirmed by Dumas, while his atomic weight for arsenic was corroborated by Pérouze and Dumas. The metals of the alkaline earths—barium, strontium, calcium and magnesium, which were isolated by Davy—were investigated by Berzelius, Marignac and Dumas, who determined their atomic weights. Recently Winkler found that magnesium is an excellent reducing

agent for metallic oxides. Cobalt and nickel have been the subject of researches of an important nature, mainly because of the remarkable compounds they form—*e.g.*, nickel tetra-carbonyl and the ammonio-cobaltic compounds. Nickel is now extensively used in metallurgy, especially in the production of nickel steel.

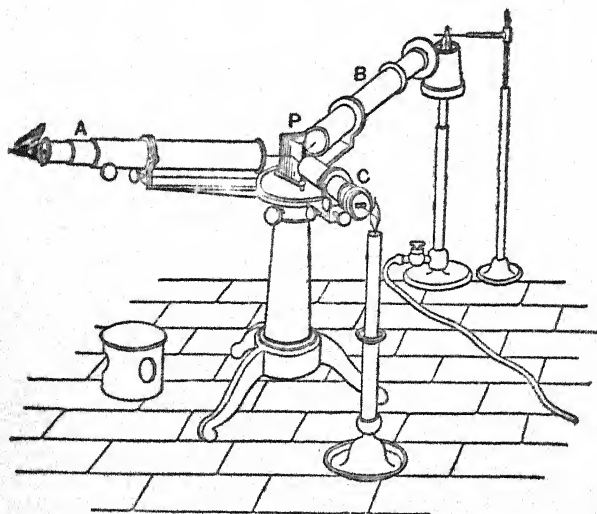


Fig. 24 —SPECTROSCOPE.

A., telescope, through which the spectrum is seen magnified; B., collimator-tube; C., tube containing a scale; P., prism for dispersing the light.

The rarer metals have, of course, received considerable attention. Uranium, which was discovered by Klaproth in 1798, was investigated further by Péligot, Roscoe and, lately, by Zimmermann. Molybdenum and tungsten, isolated respectively by Hjelm and d'Elhujar, have become

better known, and the acids and the complicated salts of these have been studied by Scheibler, Marignac, Friedheim and Gibbs. Uranium, and, particularly, tungsten and molybdenum are now employed extensively as steel-hardening materials. Uranium compounds are also used in dyeing and ceramics.

Titanium, zirconium and thorium have now become, in the form of various compounds, particularly the oxide, of practical importance. Thorium was discovered by Berzelius in 1828; its oxide, thoria, is applied in the manufacture of Welsbach gas mantles, which consist essentially of a web of 99 per cent. thoria and 1 per cent. cerium oxide. Titanium is employed for the manufacture of special alloys, and zirconium, as zirconia, is made use of both in gas and electric illumination. Germanium, an element which resembles these in some respects, was discovered by Winkler in 1886 in a Freiberg silver ore.

The element vanadium, which was discovered by Del Rio in 1801, was isolated by Roscoe in 1867. He also investigated its compounds carefully, determining its different stages of combination with oxygen and chlorine. This metal, which is widely distributed, is utilized in the production of sheet and tool steel and armor plates. Tantalum, a related metal, which, along with columbium, or niobium, was examined exhaustively by Blomstrand and Marignac, is used in alloys to make small springs and anvils, and in the metallic form to make special incandescent electric light filaments.

The metals of the platinum group—platinum, palladium (Wollaston, 1803), rhodium (Wollaston, 1804), iridium (Tennant, 1803), osmium (Tennant, 1803), and ruthenium (Claus, 1844)—have been given careful consideration by chemists. Platinum is used extensively in making chemical apparatus, especially crucibles and stills; and osmium and iridium have recently come into use as filaments for incandescent lamps.



About fifteen years ago the number of the chemical elements was enlarged by two gases of great theoretical interest—argon and helium.

As early as 1785, Cavendish had noticed that a residue of about 0.6 per cent. remained when the nitrogen and oxygen were removed from air, and in 1894 Rayleigh discovered that nitrogen from the atmosphere was 0.5 per cent. heavier than nitrogen prepared chemically. Rayleigh and Ramsay then prepared large quantities of this atmospheric residue and found it to be a gas different from nitrogen. They called it 'argon' from the Greek 'argos,' lazy.

Helium was discovered by Ramsay in 1895 in the mineral cleveite. It had already been found to exist in the chromosphere of the sun by Janssen in 1868, and his observations were confirmed by Frankland and Lockyer. Helium, primarily obtained by heating cleveite with sulphuric acid, and since found in small quantity—often together with argon—in the minerals uraninite, malacone, etc., as well as in the gases from some mineral water springs, is, like argon, inert and indifferent. Up to now, in spite of persistent effort, no compound of either argon or helium has been prepared. And, further, altho many diffusion experiments with both gases have been carried out, with the object of seeing whether they were really elementary, the densities of both have remained unaltered—i.e., it has been found impossible to subdivide them by diffusion into two or more components. From the ratio of the specific heats at constant volume and constant pressure, it follows that the molecule and atom are identical in both argon and helium—i.e., that the gases are monatomic; and this applies also to the other more recently discovered gases of the air—krypton, neon and xenon.

These were separated from liquid air in 1898 by Ramsay and Travers. The atomic weights of these gases and the proportions in which they are present in the air are as follows:



	Atomic Weight.	One Part by Volume in Air.
Helium	4	2,450 volumes
Neon	20	808 "
Argon	39.9	105 "
Krypton	81.8	746,000 "
Xenon	128	3,846,000 "

Since the interest attached to these gases has been recently augmented by the discovery of Ramsay and Soddy that radium emanation eventually changes, at least in part, into helium, and since Ramsay has shown that when the radium emanation decays in the presence of water neon is produced, and that argon results when the decay takes place in the presence of water containing a copper salt in solution, the radioactive elements may be conveniently referred to here.

Henri Becquerel found in 1896 that compounds of uranium spontaneously and continuously emit some radiation which, among other properties, has that of making air a conductor of electricity. This effect, the quantity of which can be determined with great accuracy, was used by Mme. Sklodowska Curie to measure the amount of radiation produced by various compounds of uranium and of thorium, which latter had been found by Schmidt to emit the same kind of radiation.

She subsequently tested a large number of rocks and minerals, and found that certain minerals which contained uranium and thorium—*e.g.*, pitchblende (oxide of uranium), chalcocite (double phosphate of copper and uranium)

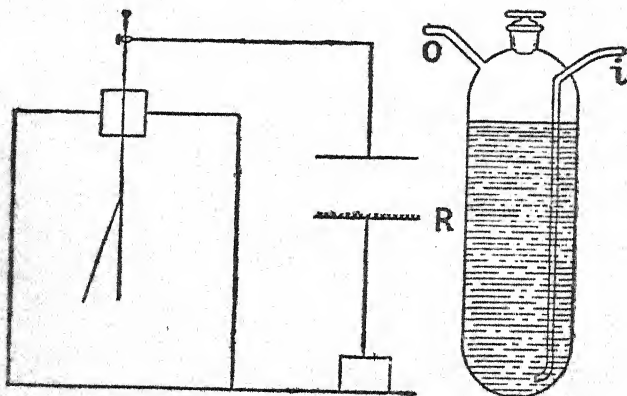


Fig. 25 — APPARATUS EMPLOYED IN STUDYING RADIOACTIVITY.

1., spinthariscope. In this instrument a particle of radium nitrate is placed near a fluorescent screen of zinc sulphide; when this is examined with a high-power magnifier a scintillating appearance of great brilliancy is observed, giving the appearance of a "turbulent luminous" sea. The small set-screw regulates the distance between the screen and the radium, thus allowing of a variation in the effects produced. 2., radium cell. 3., electroscope with discharging plates. 4., tube for the removal of radium emanation from solution. R = radium salt in solution, i = inlet tube for air stream, and O = outlet tube for air.

—possess radio-activity much greater than that “theoretically” due to the amount of uranium present.

Mme. Curie therefore inferred that, “It appeared probable that if pitchblende, chalcocite, etc., possess so great a degree of activity, these substances contain a small quantity of a strongly radio-active body, differing from uranium and thorium and the simple bodies actually known. I thought that if this were indeed the case, I might hope to extract this substance from the ore by the ordinary methods of chemical analysis.”

The investigation was consequently pursued, and, with the assistance of her husband, Pierre Curie, and Gustave Bémont, Mme. Curie commenced the laborious treatment of the residue remaining after the extraction of the uranium from pitchblende, a large quantity of which had been placed at her disposal by the Austrian Government, and finally separated the salts of radium in 1898. While endeavoring to isolate radium, Mme. Curie discovered polonium, and other investigators—Debiere, Giesel, Marckwald and Hofmann—have given the names of actinium, emanium, radio-tellurium and radio-lead to similar substances, the two last being possibly products of the spontaneous change in radium. Among those who have worked with success upon the problem of radio-activity, Elster and Geitel, Rutherford, Soddy and Ramsay may be mentioned here.

Radium maintains a temperature one or more degrees above that of the atmosphere, injures the eyes, and disorganizes the flesh when kept long in contact with it. Its peculiar properties have been explained in various ways. The most plausible suggestion is that atoms of high atomic weight slowly disintegrate into ultimate corpuscles or particles, and that this decomposition is attended with the development of great energy.

The successive disintegration of the radium atom as exemplified by the disintegration products is shown in the following table, which represents, according to Ernest

Rutherford, the complete radium series as at present known:

Element.	Radiation emitted.	Period.	Range of $\alpha$ particles in air at normal pressure.
Radium . .	$\alpha$ particles	2000 years	3.5 cms.
↓			
Emanation .	$\alpha$ particles	3.8 days	4.3 cms.
↓			
Ra. A . . .	$\alpha$ particles	3 minutes	4.8 cms.
↓			
Ra. B . . .	$\beta$ particles	26 minutes	—
↓			
Ra. C . . .	$\alpha$ and $\beta$ particles $\gamma$ rays	19 minutes	7.06 cms.
↓			
Ra. D . . .	?	40 years	—
↓			
Ra. E . . .	?	6 days	—
↓			
Ra. F . . .	$\beta$ particles	4.5 days	—
↓			
Ra. G . . .	$\alpha$ particles	140 days	3.86 cms.
↓			

It appears that uranium is the source of radium, and Boltwood has recently announced the immediate parent of radium, "ionium." Radium resembles barium chemically and, according to Mme. Curie and Thorpe, it has an atomic weight of 226.5. Several observers have demonstrated that it possesses a characteristic spectrum, and consequently, notwithstanding its disintegration and peculiar conduct, radium is regarded as a chemical element,

owing to an affidavit among chemists to recognize a body as a chemical element when, under proper conditions, it possesses a definite atomic weight and exhibits a spectrum containing characteristic and novel lines.

In 1823, Mitscherlich discovered the existence of sulphur in two different crystalline varieties—rhombic and oblique, and a third variety, the plastic form, was also known. Frankenheim learned that by heating and cooling, these varieties could at definite temperatures be converted into one another, and in describing these phenomena the term isomerism was employed, to which, however, Berzelius published an objection in 1841. To quote from his 'Jahresbericht' for that year:

"I feel compelled to call attention to the fact that the word isomerism, which is applied to different substances composed of an equal number of atoms of the same elements, is not compatible with the view as to the cause of the different properties exhibited by the various modifications of sulphur, carbon, silicon, etc. . . . While the term still lends itself to the expression of the relation between ethylformate and methylacetate, it is no longer suitable in the case of simple substances which assume different properties, and it might be desirable to substitute for it a better chosen term—*e.g.*, allotropy, or allotropic modifications. In accordance with these views there can be more than one cause for that which we call isomerism, namely:

(1) Allotropy, in which case . . . the difference between the sulphides of iron is due to the fact that they contain different modifications of sulphur.

(2) Differences in the relative position of the atoms in the compound, of which the two kinds of ether (ethylformate and methylacetate) are so striking a proof.

(3) A combination of (1) and (2)."

Since then the term allotropy has been in constant use, and numerous allotropic phenomena have been observed,

particularly among the non-metals. The allotropism of carbon was the first observed example (1773), and its modifications exhibit marked points of difference; for instance, comparing diamond and graphite:

		Crystallographic System	Optical Properties	Chemical and Physical Properties	Specific Gravity	Hardness
Carbon	Diamond	Cubic	Colorless, transparent; high refractive index, $\mu = 2.417$	Non-conductor of heat and electricity; not attacked by oxidizing agents; ignition temperature $760^{\circ}$ to $875^{\circ}$	3.52	10
	Graphite	Hexagonal? Oblique?	Opaque	Good conductor of heat and electricity; oxidized to graphitic acid; ignition temperature $575^{\circ}$ and above	2.25	1

When amorphous carbon (coal, peat, lampblack, etc.) and diamond are heated, they pass into the graphitic variety, and graphite is now produced in large amounts by heating carbon to a high temperature ( $4,000^{\circ}$  C.) by an alternating electric current. Henri Moissan (1852-1907), an eminent French chemist, succeeded in preparing synthetic diamonds by dissolving pure sugar charcoal in molten pure iron and suddenly cooling the mass by plunging it into water; and three English chemists, Sir F. A. Abel, W. H. Noble and Sir William Crookes, obtained diamonds by exploding some of the high explosives in steel bombs, the liquid carbon produced crystallizing as it cooled. However, no diamonds have thus far been produced of commercial size or amount.

The most peculiar, as well as noteworthy, example of allotropism is afforded by the conversion of oxygen into ozone. Ozone was first noticed by Van Marum in 1785

in electrified air. In 1840, C. F. Schönbein called attention again to this substance, discovered its oxidizing action, and showed that it was produced in the electrolysis of water and in the slow combustion of phosphorus and sulphur. He gave it the name "ozone," which means a smell. The investigations of Marignac, De la Rive, Becquerel, Tait, Fremy, Andrews and Brodie have proved it to be modified oxygen. Its density was determined by Soret in 1860. The latter, and before him Andrews, proved that the ozone molecule contains three atoms of oxygen, while a molecule of the latter is made up of two atoms. Ozone is now used in the sterilization of water.

Among other allotropic modifications those of selenium and phosphorus are of interest. Berzelius investigated the allotropes of selenium, and those of phosphorus were studied by Berzelius, Schrötter, Hittorf and Schenck. Schrötter discovered the red variety in 1845, and Hittorf found that it could be transformed into a metallic modification. Several additional allotropes of sulphur have been discovered in late years, and the fact that many metals can also exist in allotropic forms has been clearly demonstrated—*e.g.*, colloidal gold, silver, platinum and mercury.

The list of the compounds of the elements was greatly extended from the time of Lavoisier, particularly with the discovery of new acids and the growing knowledge of the different basicity of the various acids. It is important to mention some of the discoveries of moment.

In 1818, one of the most interesting of inorganic compounds was discovered by Thénard. He proved that water was not the sole oxide of hydrogen, but that another—peroxide of hydrogen, but which he termed "oxygenated water"—may be prepared. This compound plays a prominent rôle in many processes of nature, and is now prepared in quantities, by treating barium dioxide with sulphuric acid, for disinfecting and bleaching purposes.

The list of the halogen acids was completed prior to



1820. Gay-Lussac and Balard studied hydriodic and hydrobromic acids; the former, Davy and Faraday investigated hydrochloric acid; while Thénard, Gay-Lussac and Berzelius contributed greatly to an intimate knowledge of hydrofluoric acid. In 1869, Gore and Nicklés continued the investigation of anhydrous hydrofluoric acid, and the latter lost his life through its action. Gore and Frémy established its composition, but, as before mentioned, the element fluorine was not isolated until 1886.

The oxygen compounds of chlorine, iodine and bromine have been given much attention since the commencement of the nineteenth century. The work of Gay-Lussac on chloric acid, Balard on hypochlorous acid, Millon on chlorous acid, and Davy and Stadion on chlorine peroxide, was exceedingly valuable and led to researches which firmly established the composition of these bodies. The oxygen compounds of iodine received careful attention in the hands of Davy and Magnus, and the latter discovered iodic acid, the principal compound of that halogen.

Following Gay-Lussac's discovery of "hyposulphurous acid" in 1813 and dithionic acid in 1819, little attention was given to the compounds of sulphur and oxygen until the fourth decade, when the thio-acids, which contain more sulphur and are more closely related to sulphuric acid, were recognized. More recently the early known oxides of sulphur—sulphur dioxide and sulphur trioxide—have received several additions in sulphur sesquioxide, sulphur tetroxide and sulphur heptoxide. Sulphuric acid, the most important of all chemicals, is used in enormous quantities in the industries, and its manufacture has been immensely developed. Over two million tons were used in the United States in 1908.

The very poisonous compounds of hydrogen with phosphorus, arsenic and antimony—phosphine, arsine and stibine—were given considerable attention during the first and second decades of the modern period. Phosphine, or hydrogen phosphide, was discovered in 1783 by Gen-

gembre, and its composition was studied by Davy. Rose continued its investigation at a later date. Arsine was prepared in a pure state by Soubeiran; Gehlen fell a victim to its toxic action in 1815.

Phosphorous and phosphoric acids were known to Lavoisier, but their constitution was not established until a much later period. It was upon the relations which Gay-Lussac, Stromeyer and Graham found existing between the ortho-, pyro and meta-phosphoric acids, that Liebig founded his theory of polybasic acids, which marked such an important step forward in chemistry.

The important compound hydroxylamine, which may be regarded as ammonia in which a hydrogen atom has been replaced by hydroxyl (OH), was discovered by Lossen in 1865. It has led to a knowledge of many remarkable organic compounds. Similarly, the analogous compound, hydrazine, which was first prepared by Curtius in 1887, has entered into the preparation of a series of interesting compounds; for example, the hydrazones and hydrazides. It is an exceedingly powerful reducing agent.

Of the simple carbon compounds, the greater number were discovered in the first decade. Carbon disulphide, which was accidentally discovered by Lampadius in 1796 while heating pyrites with coal, was accurately examined by Vauquelin in 1812. It is now prepared in an electric furnace, by conducting sulphur vapor over heated carbon, and finds extensive use as a solvent. Carbonyl chloride, or "phosgene gas," was discovered by Davy in 1811, and carbon oxysulphide by von Than quite recently. The compounds of carbon with certain metals—carbides—are now of great technical importance. In 1808, Davy discovered potassium carbide, the first described in chemical literature, and in 1862 Wöhler prepared calcium carbide, now one of the most important on account of its use in the generation of acetylene and in the manufacture of calcium cyanamide, a new constituent of fertilizers. Cal-

cium carbide has, since 1844, been prepared by fusing limestone and carbon together in an electric furnace.

Before closing this brief resumé of some of the advances made in the knowledge of chemical compounds mention must be made of the metallic peroxides, hydrides and nitrides.

Sodium peroxide, which was discovered by Gay-Lussac, is now used extensively under the name "oxone" as a bleaching and oxidizing agent, and calcium peroxide, discovered by Gay-Lussac and Thénard, is used in dentistry. The discovery of the hydrides belongs to the present day; among the most important of these is calcium hydride, "hydrolite," which is used for generating hydrogen. The metallic nitrides, as magnesium, calcium, boron and lithium nitrides, have only lately been investigated carefully, but may become of great importance.

Numerous important chemical and physical facts were learned concerning the gaseous bodies, especially during the second, third and seventh decades, and the experiments which were conducted with a view of liquefying gases are of the highest import, more particularly with regard to the production of liquid air and its application to researches at low temperatures.

The experiments of Davy and Faraday, in which the gases were generated in curved closed glass tubes and cooled to about  $-20^{\circ}$  C. in a freezing mixture, resulted in the liquefaction of all the common gases, with the exception of hydrogen, nitrogen, oxygen, methane, carbonic oxide and nitric oxide. In 1834, Thilorier liquefied carbon dioxide in considerable quantities and obtained the solid; he was the first to operate on a large scale, and subsequent investigators made use of many of his observations. Between the years 1844 and 1855, Natterer studied the relationship of pressure and volume over wide ranges of pressure, and in 1852 he exposed hydrogen to a pressure of 2,790 atmospheres, but was unable to effect its liquefaction.

It was only in 1877 that Raoul Pictet and Lewis Cailletet succeeded, almost simultaneously, in liquefying the majority of the so-called permanent gases. Their success was due to a recognition of the fact that reduction of temperature was necessary as well as pressure, but it was not possible by the aid of the methods and appliances which they employed, to obtain the liquids in large amounts and

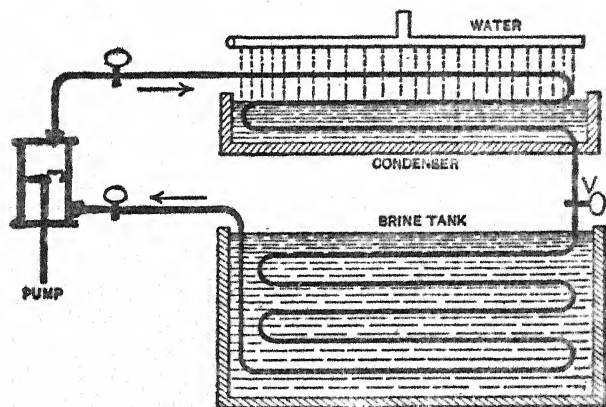


Fig. 26 —AMMONIA ICE-PLANT.

Ammonia gas is pumped under great pressure into the condenser pipes, which are cooled by a shower of cold water. The liquefied ammonia is admitted through the expansion-valve *v* to the coils in the brine tank. The cold produced by the volatilization and expansion of the ammonia lowers the temperature of the brine to about  $-20$ . The water to be frozen is placed in prismatic vessels and lowered into the brine.

to determine their physical constants. This was accomplished by Wroblewsky, a chemist in Cracow, and he and Olszewsky first obtained quantities of oxygen and nitrogen in the liquid state, and described many of their properties. These two investigators share with Dewar, an English chemist, the honor of having first devised practical methods for the production of liquid air in quantity; and in

1896 C. Linde in Germany and W. Hampson in England constructed technically efficient forms of apparatus for producing liquid air.

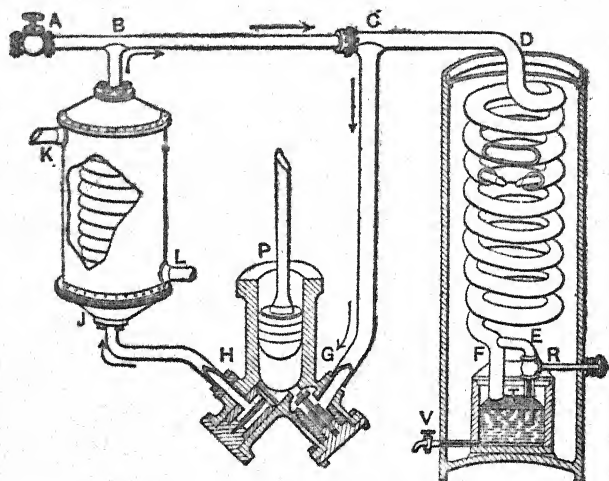


Fig. 27 — APPARATUS FOR LIQUEFYING AIR.

Linde's apparatus consists essentially of a pump (P.), a cooler (J.), a double spiral tube surrounded with non-conducting material (D.), and a reservoir for the liquid (T.). The double tube, which is several hundred feet in length, is so arranged that the air in the inner tube is subjected to a pressure of 200 atmospheres, while the pressure in the outer tube is only 20. The pump draws air from the outer and forces it into the inner tube. The air passes through the cooler to remove the heat due to compression and is then allowed to flow through a cock (R.) into the reservoir, where it is cooled by its sudden release from pressure and its rapid expansion. In a little while the air reaches the liquefying temperature and slowly collects in the receiver.

Liquid air has not as yet, however, found any technical application upon a large scale. Nearly pure oxygen is obtained from it very cheaply, and the attempt has been

made to apply it in the manufacture of explosives, but, so far, liquid air has achieved the most important results in chemical research.

In the first place, it must be mentioned that Dewar, by its aid, has succeeded in liquefying hydrogen, and in obtaining air, oxygen and hydrogen in the solid state; and that in doing so he has achieved almost everything that can

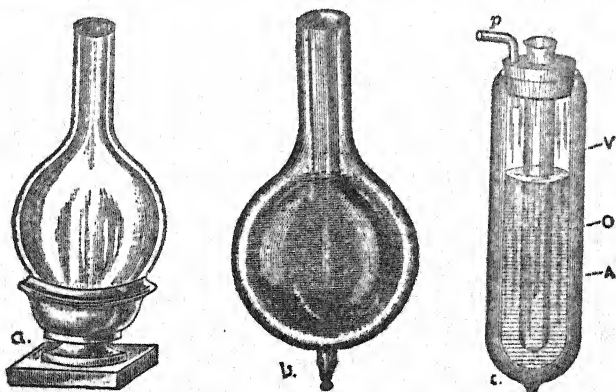


Fig. 28 —CRYOGENIC APPARATUS.

Some apparatus employed in experiments with liquid air. a., Dewar bulb, a vessel of double walls separated by a vacuum; the walls of the evacuated space are silvered to reduce the heating effect of transmitted light. Vessels of this type are used as containers for liquid air. b., another view of same. c., apparatus for obtaining liquid oxygen in the laboratory.

be done in this direction. However, he is at present attempting to reach the so-called absolute zero.

The results that have been obtained by means of this agency with respect to the discovery of the "noble gases" are of greater importance. Since these have been described, it only remains to be stated that Onnes, in his cryogenic laboratory in Leyden, has recently announced that he has liquefied helium and that it boils at  $-268.5^{\circ}\text{C}$ .



## CHAPTER XV

### THE ATOMIC WEIGHTS AND THE PERIODIC LAW

IN a preceding chapter an attempt was made to trace the early development of the atomic theory, and later it was shown how this theory became a necessity for the development of organic chemistry.

It had fallen into disfavor because of the difficulties encountered by Berzelius and others in distinguishing between atoms and molecules; but much light was thrown upon this and other matters as the chemistry of the compounds of carbon was better understood; and the fact that the dominant doctrine of the new chemistry quietly assumed the truth of Dalton's theory in all its important particulars was reflected upon the older chemistry, so that this great theory became the basis for it all.

The old confusion between atoms and equivalents was not entirely done away with until after Frankland's investigations of the organo-metallic bodies, yet in 1846 Laurent had clearly distinguished between atom, molecule and equivalent, and his definitions are still current. He stated that "the atom of M. Gerhardt represents the smallest quantity of a simple body which can exist in a combination; my molecule represents the smallest quantity of a simple body which must be employed to perform a chemical reaction."

This definition of a molecule was employed until quite lately in general, but in 1888 Lothar Meyer pointed out that it was insufficient. Gerhardt defined "equivalent" as follows:



"According to our views, the conception of equivalent implies that of similarity of function; it is known that the same element can play the part of one or other of several very different elements, and it may happen that to each of these different functions corresponds a different weight of the first element."

Seven years previously, in 1842, when he had not arrived at a clear distinction between "equivalent" and "atomic weight," Gerhardt had doubled the equivalents of carbonic acid and of water, and in 1843 he followed this up by doubling the values of the symbol weights used by French chemists ( $H = 0.5$ ,  $O = 8$ ,  $C = 6$ , etc.), rendering them thereby identical with Berzelius' atomic weights. The reasons for this change were derived from the study of chemical reactions. He found that the amounts of water, carbonic acid, ammonia and sulphurous acid evolved in the interactions between the quantities of organic compounds represented by the formulæ assigned to them on chemical grounds, were always two (or multiples of two) equivalent weights of  $H_2O$ ,  $CO_2$ ,  $SO_2$ , when  $H = 0.5$ ,  $O = 8$ ,  $C = 6$ ,  $S = 16$ .

Both Gerhardt and Laurent expressed sound views on the selection of atomic weights. They recommended the choice of such of these as were in agreement with the requirements of the law of isomorphism, the law of Avogadro and the law of heat capacity, and which above everything are chemically adequate. However, apparently the chemical public was not yet ready for the change. In his great text-book on organic chemistry, the publication of which was begun in 1853, Gerhardt retained Gmelin's equivalent-weight notation. He is reported to have said in private conversation that unless he had done so no one would have bought the work; in the introduction to the book the matter is put more formally:

"I have even sacrificed my notation, retaining the old formulæ the better to show by example how irrational they

are, and leaving to time the consummation of a reform which chemists have not yet adopted."

Confusion continued to reign for some time longer. The terms equivalent, atomic weight, molecular weight were used and abused in every conceivable sense; sometimes even employed as synonymous.

About the middle of the century two units or standard elements were in use for the determination of combining weights. Dalton had suggested hydrogen as unity, and this standard was adopted by Gmelin and many others. Wollaston and Berzelius took oxygen as the standard, Wollaston giving it the value 10, and Berzelius using it as 100; Thomson had given it the value 1. The standard of Berzelius was the accepted one for a long time, but about 1842 a return was made to the standard of Dalton. It was in this year that Dumas, whose atomic weight determinations are classical, redetermined the ratio oxygen: hydrogen from the composition of water, and had ascertained it to be 15.96:2, and had expressed his belief that the true value was probably 16:2. His number, which in the same year was confirmed by the results of Erdmann and Marchand, was for a long time considered as extremely exact.

However, the work of Jean Servais Stas (1813-1891) soon after furnished numbers for the combining weights of a large number of elements which had all been determined by direct reference to 16 of oxygen, and the accuracy of which was far superior to that of the ratio oxygen: hydrogen. Indirectly he had obtained for hydrogen in terms of oxygen = 16.00, the value 2.02. Though not attaching special importance to this result, Stas asserted that the composition of water was not known with sufficient accuracy for hydrogen to be a suitable standard, and he expressed himself in favor of 16 of oxygen. Since, however, 16.00 was then generally accepted as the exact combining weight of oxygen in terms of the hydrogen standard, Stas' recommendation involved no recalculation;

that is, no change in practice, only a change in theory desirable from the point of view of future possibilities. The adoption of the oxygen standard advocated would have meant that if a redetermination of the composition of water should lead to a change in the value of the ratio oxygen : hydrogen, the effect of this would only be an alteration of the value used for the combining weight of hydrogen, and not the necessity of a recalculation and a consequent change of all the combining weight values determined directly in terms of oxygen. Stas' suggestion, which it must be admitted was not pressed strongly, did not receive much support.

All the work of Stas was monumental in the care taken to secure accuracy. The determinations of atomic weights by him of importance were those of silver, potassium, sodium, lithium, lead, chlorine, bromine, iodine, sulphur, nitrogen and oxygen.

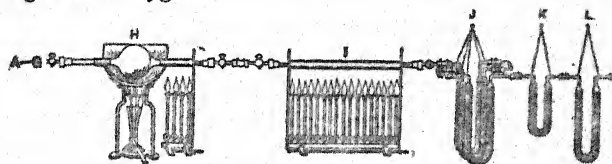


Fig. 29 — APPARATUS OF STAS.

Apparatus used by Stas for the complete analysis of silver iodate.

Much of this work was carried out to prove or disprove the correctness of Prout's hypothesis, and Stas concluded as follows: "I have arrived at the absolute conviction, the complete certainty, as far as it is possible for a human being to attain to certainty in such a matter, that the law of Prout, together with M. Dumas' modifications, is nothing but an illusion, a mere speculation definitely contradicted by experience."

In 1860, J. C. Marignac (1817-1894), who had determined the atomic weights of a number of elements, pub-

lished a paper in support of what he termed Prout's "law." He observed that " . . . the differences between the results obtained by M. Stas and those required by the law of Prout are certainly very small, but they are considerably greater . . . than the greatest differences between the results obtained in each set of experiments."

The results referred to, as well as those of Marignac himself, are appended:

	Stas (1860).	Marignac.	Prout.
Silver .....	107.943	107.921	108
Chlorine .....	35.46	35.456	35.5
Potassium .....	39.13	39.115	39
Sodium .....	23.05	....	23
Ammonium .....	18.06	....	18
Nitrogen .....	14.041	14.02	14
Sulphur .....	16.037	....	16
Lead (synthesis of sulphate).	103.453	....	103.5
Lead (synthesis of nitrate)..	103.460	....	103.5

Marignac reasoned from Stas' results that Prout's hypothesis was substantiated rather than disproved. He employed the two arguments of the Proutians, that Stas' numbers were very close approximations to whole numbers and hence could be considered as such, and that those approximations were too numerous to be accidental. This fatal error of rounding off fractions into whole numbers was the very thing which misled Prout at the beginning and with him there was far more excuse for it. Marignac further said that should future determinations of other elements give similar approximations he would feel assured of the existence of some fundamental cause which brought about the multiple relation of the atomic weights and subordinate causes which modified it. He thought that Prout's Law deserved to rank with that of Gay-Lussac or of Mariotte.

In another place Marignac referred to Prout's Law as

one of those not absolute but only approximate laws, like many other natural laws.

From 1888 onward, there appeared in quick succession redeterminations of the ratio oxygen:hydrogen, all demonstrating that Dumas' experimental number 15.96 was too high; but in the meantime Lothar Meyer and Seubert, strong champions of the hydrogen standard, had made this value the basis of very popular atomic weight tables. The new data did not provide a sufficiently reliable number to make recalculations of all the other values desirable, and the obvious way out of the difficulty, the use of the tables of Ostwald in which the 16.000 oxygen standard was used, was not generally accepted. As a result two tables of atomic weights, one based on  $O = 16$  and the other on  $O = 15.96$ , were in use until quite recently.

From the year 1896 onward, K. Seubert exerted himself to effect a general agreement with regard to the basis upon which all atomic weights should be founded, and in 1900 an International Atomic Weights Commission was appointed for the purpose of settling the question. The result of their deliberations has been to make oxygen ( $O = 16$ ) the "official" basis instead of hydrogen ( $H = 1$ ); the hydrogen unit is, however, often preferred still, both in practical work and in teaching. The main ground for the Commission's taking oxygen as the foundation is the fact—originally brought forward by Berzelius—that by far the greater number of the atomic weights have been derived from compounds of oxygen and not from compounds of hydrogen.

Among the chemists other than those mentioned whose efforts were directed to improving the methods of determining atomic weights may be mentioned Turner, Penny, Marchand, Pérouze, De Ville, and Scheerer. Recently Morley and Richards have done noteworthy work.

The most recent table of International Atomic Weights is as follows:

O = 16		O = 16	
Aluminium....Al	27.1	Lithium .....Li	7.00
Antimony ...Sb	120.2	Lutecium ....Lu	174.0
Argon .....A	39.9	Magnesium ..Mg	24.32
Arsenic .....As	74.96	Manganese ...Mn	54.93
Barium .....Ba	137.37	Mercury .....Hg	200.0
Bismuth .....Bi	208.0	Molybdenum..Mo	96.0
Boron .....B	11.0	Neodymium ..Nd	144.3
Bromine .....Br	79.92	Neon .....Ne	20.0
Cadmium ....Cd	112.40	Nickel .....Ni	58.68
Cæsium .....Cs	132.81	Nitrogen ....N	14.01
Calcium .....Ca	40.09	Osmium .....Os	190.9
Carbon .....C	12.00	Oxygen .....O	16.00
Cerium .....Ce	140.25	Palladium ....Pd	106.7
Chlorine .....Cl	35.46	Phosphorus ...P	31.0
Chromium ...Cr	52.0	Platinum ....Pt	195.0
Cobalt .....Co	58.97	Potassium ...K	39.10
Columbium ..Cb	93.5	Praseodym'm. Pr	140.6
Copper .....Cu	63.57	Radium .....Ra	226.4
Dysprosium ..Dy	162.5	Rhodium ....Rh	102.9
Erbium .....Er	167.4	Rubidium ....Rb	85.45
Europium ...Eu	152.0	Ruthenium ...Ru	101.7
Fluorine.....F	19.0	Samarium ...Sa	150.4
Gadolinium ..Gd	157.3	Scandium ....Sc	44.1
Gallium .....Ga	69.9	Selenium ....Se	79.2
Germanium ..Ge	72.5	Silicon .....Si	28.3
Glucinum ....Gl	9.1	Silver .....Ag	107.88
Gold .....Au	197.2	Sodium .....Na	23.00
Helium .....He	4.0	Strontium ...Sr	87.62
Hydrogen ...H	1.008	Sulphur .....S	32.07
Indium .....In	114.8	Tantalum ....Ta	181.0
Iodine .....I	126.92	Tellurium ....Te	127.5
Iridium .....Ir	193.1	Terbium .....Tb	159.2
Iron .....Fe	55.85	Thallium ....Tl	204.0
Krypton .....Kr	83.0	Thorium .....Th	232.42
Lanthanum ..La	139.0	Thulium .....Tm	168.5
Lead .....Pb	207.10	Tin .....Sn	119.0



	O = 16		O = 16
Titanium .... Ti	48.1	Ytterbium ... Yb	172.0
Tungsten .... W	184.0	(Neoytterbium)	
Uranium ..... U	238.5	Yttrium ..... Y	89.0
Vanadium ... V	51.2	Zinc ..... Zn	65.37
Xenon ..... Xe	130.7	Zirconium ... Zr	90.6

Reverting to the middle of the past century, one finds that much of the credit of removing the difficulties attending the determination of the atomic weights, and of transferring them to a more substantial foundation than had hitherto been in use, is due to Stanislao Cannizzaro (1826—). It was he who, by his criticism in a paper entitled 'Sunto di un Corso de Filosofia Chimica' ('Outlines of a Course of Chemical Philosophy') (1858), elucidated the methods employed for arriving at the relative atomic weights of the elements. He recognized, as especially reliable, the deduction of these values from the vapor densities of chemical compounds—a method now in universal use.

Cannizzaro's paper began as follows (Freund):

"It seems to me that the progress of chemistry within the last year has served to confirm the hypothesis of Avogadro, Ampère and Dumas concerning the similar constitution of gaseous substances; namely, the assumption that equal volumes of gases, whether elementary or compound, contain an equal number of molecules. But they by no means contain an equal number of atoms, the reason for this being that the molecules of different substances, or even of the same substance in the different states which it can assume . . . may consist of a different number of atoms of the same or of different kinds. In order to bring my pupils to this same conviction I have let them follow the same path that had led me to it; namely, that of the historical examination of chemical theories.

"I begin by showing how from a consideration of the physical properties of gases, together with Gay-Lussac's



law concerning the relation between the volume of a compound and that of its constituents, there has arisen, as it were, of itself that hypothesis which was first enunciated by Avogadro and shortly afterward by Ampère. While expounding in detail the line of argument followed by these two physicists I proceed to prove that it is not in contradiction to a single known fact, provided only that we do as they did: (1) Distinguish between the molecules and the atoms; (2) avoid confounding the criteria for comparing the weights and numbers of molecules with those employed for ascertaining the weights of atoms; (3) abandon the erroneous view that while the molecules of a compound may consist of any number of atoms, those of the different elements must consist of one atom only, or at any rate of an identical number of atoms."

He then discussed molecular weight determinations and showed that the hypothesis of Avogadro was a guide in such work. His argument in favor of making the weight of half the hydrogen molecule the standard met with favor and acceptance. Turning from the molecule to the atom, Cannizzaro showed that the law of Dulong and Petit, and Avogadro's hypothesis were a guide in the determination of the atomic weights. To quote further from his paper:

"We next proceed to the investigation of the composition of the molecules. Whenever the substance cannot be decomposed, it must be assumed that the whole weight of its molecules is composed of one kind of matter only; but if the substance is a compound we analyze it and thereby determine the invariable ratio by weight of its constituents, and we then proceed to divide the molecular weight into parts proportional to those of the relative weights of the constituents and thus obtain the quantities of the elements contained in a molecular weight of a compound, all of them referred to the same unit in terms of which all molecular weights are expressed. According to this method I compile the table of molecular composition which follows:

# THE ATOMIC WEIGHTS

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Name of the substance	Weight of one volume, or molecular weight referred to the weight of a half hydrogen molecule = 1	Weights of the constituents of one volume or of one molecule, all referred to the weight of a half hydrogen molecule = 1
Hydrogen	2	2 Hydrogen
Oxygen	32	32 Oxygen
Electrified oxygen	128	128 Oxygen
Sulphur under 1,000°	192	192 Sulphur
Sulphur above 1,000°	64	64 Sulphur
Phosphorus	124	124 Phosphorus
Chlorine	71	71 Chlorine
Bromine	160	160 Bromine
Iodine	254	254 Iodine
Nitrogen	28	28 Nitrogen
Arsenic	300	300 Arsenic
Mercury	200	200 Mercury
Hydrochloric acid	36.5	35.5 Chlorine 1 Hydrogen
Hydrobromic acid	81	80 Bromine 1 Hydrogen
Hydriodic acid	128	127 Iodine 1 Hydrogen
Water	18	16 Oxygen 2 Hydrogen
Ammonia	17	14 Nitrogen 3 Hydrogen
Arsenine	78	75 Arsenic 3 Hydrogen
Phosphine	35	32 Phosphorus 3 Hydrogen
Mercurous chloride	235.5	35.5 Chlorine 200 Mercury
Mercuric chloride	271	71 Chlorine 200 Mercury
Arsenic chloride	181.5	106.5 Chlorine 75 Arsenic
Phosphorous chloride	138.5	106.5 Chlorine 32 Phosphorus
Ferric chloride	325	213 Chlorine 112 Iron
Nitrous oxide	44	16 Oxygen 28 Nitrogen
Nitric oxide	30	16 Oxygen 14 Nitrogen
Carbonic oxide	28	16 Oxygen 12 Carbon
Carbonic acid	44	32 Oxygen 12 Carbon
Ethylene	28	4 Hydrogen 24 Carbon
Propylene	42	6 Hydrogen 36 Carbon
Acetic acid	60	4 Hydrogen 32 Oxygen 24 Carbon
Acetic anhydride	102	6 Hydrogen 48 Oxygen 48 Carbon
Alcohol	46	6 Hydrogen 16 Oxygen 24 Carbon
Ether	74	10 Hydrogen 16 Oxygen 48 Carbon

"From this it follows that all the different quantities of hydrogen contained in the molecules of the different substances are whole multiples of the quantity contained in the hydrochloric acid molecule."

He defined the atomic weight as the weight of one atom of the element referred to the weight of the hydrogen atom taken = 1.00 (or oxygen = 16.00), and stated that it is determined by finding the least amount of the element present in the molecular weight of any of its compounds, which if these are volatile is the least amount present in 2 volumes of any of these compounds in the gaseous state.

It is unnecessary that the molecular weight of the element be known, only the molecular weights of as many volatile compounds as possible, together with the composition of these compounds expressed as parts of the molecular weights.

Chemists were thus taught to rely on Avogadro's hypothesis, all inferences drawn from which, Cannizzaro showed, "are in complete agreement with all the physical and chemical laws so far discovered." He gave as an application of Dulong and Petit's law the following:

"The specific heat of copper in the free state . . . confirms the atomistic conception of its chlorides based on analogies with the corresponding chlorides of mercury. Their composition leads us to the inference that they have the formulæ  $\text{CuCl}$  and  $\text{CuCl}_2$ , and that the atomic weight of copper is 63, a fact made apparent by the following relations:

	Ratio between the components expressed by numbers whose sum is = 100	Ratio between the components expressed by the atomic weights
Cuprous chloride	Chlorine Copper 36.04 : 63.96	35.5 : 63 = Cl : Cu
Cupric chloride	52.98 : 47.02	71 : 63 = $\text{Cl}_2$ : Cu

But the number 63 for the atomic weight, when multiplied by the specific heat of copper, gives a product nearly equal to that of the atomic weight of mercury or of iodine multiplied by their respective heats. We get:

$$\begin{array}{rcccl} 63 & \times & 0.09515 & = & 6 \\ \text{At. wt. of copper} & & \text{Spec. heat of copper.} & & \end{array}$$

By the use of this law and Avogadro's hypothesis an approximation to a correct table of atomic weights was obtained, and the road for the inception of the great natural law underlying them was opened up.

Before the atomic theory was formulated, numerical relations were proposed by Richter, the founder of Stoichiometry, between the equivalents obtained by him for the various bases and acids. This mathematical work served but little purpose beyond bringing the whole subject of his equivalents into some disrepute. Only a few years passed after the publication of the first tables of atomic weights before their inter-relation became a subject of speculation and research. In 1815 we have Prout pointing out the strange fact of their close approximation to whole numbers and boldly rounding them off into such. If they were integral multiples of hydrogen, he reasoned, then this might be the primal matter and all elements made up of it. The "Multiplen-fieber" quickly took possession of the chemical world, even of conservative, level-headed workers such as Berzelius. Enthusiastic support was given it by the English chemists especially and, when Berzelius afterward became its great antagonist, Thomson and others busied themselves in its defense. The newly organized British Association devoted its fresh energies to an examination into the condition of the various sciences and, among other inquiries, set on foot one as to the grounds for believing in what was then called and has been often so called since, Prout's Law. The result of this inquiry was adverse to the "law" and it would have been dropped, in all probability, had it not been taken up by

Marignac, Dumas and the French chemists, with certain modifications rendered necessary by the more perfect knowledge of the atomic weights.

Meanwhile, a different style of numerical regularity had been brought to the notice of chemists. In 1817, Döbereiner first noticed a strange grouping of analogous elements into threes, or triads as they soon came to be called. He said, according to Venable:

"Noteworthy relations are revealed when one examines the stoichiometrical values of the chemical elements and compounds arranged in series.

"1. Those most often found in plants have the smallest values and are the most abundant. The highest values are less widely distributed.

"2. Those corresponding in many physical and chemical properties, as iron, cobalt and nickel, have almost the same stoichiometrical value.

"3. Compounds which have like equivalent numbers are almost alike in chemical constitution."

For a long period following this paper there was no further attention given to this question, but in 1829 Döbereiner published another paper which appears to have been a result of the atomic weight determinations of Berzelius in 1825. He indicated that the atomic weight of bromine approximates the arithmetical mean of the atomic weights of chlorine and iodine, namely:

$$\frac{35.470 + 126.470}{2} = 80.970, \text{ considering } H = 1.$$

Of this mean he stated that tho somewhat greater than 78.383, the number actually found by Berzelius, it so closely approximates to it as to justify the hope that repeated accurate determinations of all the atomic weights involved will lead to a disappearance of any difference. He found similar relations for the alkaline earths, the

alkalies, and for the group comprising sulphur, selenium, and tellurium, as shown by the equations:

$$\frac{356.019 (= \text{Ca}) + 956.880 (= \text{Ba})}{2} = 656.449 (= \text{Sr}),$$

but experiment gave for strontium, regarding O = 100, 647.285.

$$\frac{195.310 (= \text{Na}) + 589.916 (= \text{K})}{2} = 392.613 (= \text{Li}),$$

but experiment gave for lithium, regarding O = 100, 390.897.

$$\frac{32.239 (= \text{S}) + 129.243 (= \text{Te})}{2} = 80.741 (= \text{Se}),$$

but experiment gave for selenium, considering H = 1, 79.263.

For more than twenty years little was added to the work of Döbereiner and no new ideas were advanced. This was in part due to imperfections in the determinations of the atomic weights and ignorance as to whether they should be written as had been done by Berzelius or many of them doubled as was done by Gerhardt.

Further, the whole question of atomic weights was in much doubt and numerical speculations concerning them would have had little significance during this period.

The first to continue the consideration of such "triads" was Dumas, who in 1851 called attention to the triads of Döbereiner, and suggested that in a series of bodies, providing the extremes are known, the intermediate bodies might be discovered, and stated that a suspicion arose as to the possibility of the intermediate body being composed of the extremes of the series and thus processes of transmutation might be hoped for.

The next year P. Kremers pointed out the existence of certain regularly ascending series among the elements, and



in 1858 he followed up the old idea of triads, arranging the elements in the form of "conjugated triads," thus:

Li = 7,	Na = 23,	K = 39.
Mg = 24,	Zn = 40,	Cd = 112.
Ca = 40,	Sr = 87.5,	Ba = 137.

In these triads we have the following proportions:  
Li: Na: K as 7: 23: 39 as Li: Mg: Ca.

Such close agreement was not found in every case, however, and in 1863 Kremers gave up the doctrine of triads.

In 1853, J. H. Gladstone announced that he found the numerical relations between the elements to be of three varieties, namely:

1. The atomic weights of analogous elements are the same.
2. The atomic weights of analogous elements are in multiple proportions.
3. The atomic weights of analogous elements may differ by certain regular increments.

He considered the doctrine of triads as partly a natural law.

The following year J. P. Cooke published a study of these numerical relations. He stated that the triads broke up natural groups of elements—a fatal blow to the doctrine—and classified the elements into six series, in each of which the number whose multiples form the differences is different and may be said to characterize the series. In the first it is nine, in the second eight, in the third six, in the fourth five, in the fifth four and in the last three. The elements were further arranged in series according to the strength of their electro-negative properties, or in other words, as their affinities for oxygen, chlorine, sulphur, etc., increased, while those for hydrogen decrease as we descend.

Cooke laid stress on the fact that his grouping demonstrated that the elements may be classified in a few series similar to the homologous series of organic chemistry. In 1858, John Mercer carried out this comparison with the



organic radicals more fully, basing his work partly on that of Max von Pettenkofer, who, while engaged on the subject of the regularities in the atomic weights, made the following comparison:

1. The equivalents of the inorganic elements, which form natural groups, show among themselves such constant differences as the equivalents of organic compound radicals which belong to natural groups.

2. The simple inorganic elements can therefore be regarded from the standpoint of the compound organic radicals.

Pettenkofer also criticized the doctrine of triads.

Lenzen and Odling were about the last chemists to attempt to develop the doctrine of the triads. The former gave twenty triads, grouping the elements according to their chemical and physical characteristics, but this classification was unsatisfactory and he suggested a division in diads, the third member forming a binding member; for example, the triads K, Na and Li became diad K, Na, and binding member Li.

The consideration of the numerical regularities of the atomic weights from the point of view of the homologous organic series, of which the ideas of Pettenkofer form a good illustration, was also taken up by Dumas, who later published his view of double parallelism. He made this comparison:

$$\begin{array}{llll} \text{N} = 14 & \text{P} = 31 & \text{As} = 75 & \text{Sb} = 122 \\ \text{F} = 19 & \text{Cl} = 35.5 & \text{Br} = 80 & \text{I} = 127 \end{array}$$

On adding 108 to the number for nitrogen we obtain that for Sb, and on adding it to F we get I, and so the addition of 61 gives us respectively As and Br. These facts teach the propriety, he says, of arranging the metals in series that shall show a double parallelism, for such a classification brings to view the various analogies existing between these elements.

None of these considerations materially advanced the subject of triads from the state in which it had been left

by Döbereiner. But, to quote from Freund's 'Study of Chemical Composition,' "When stress had once been laid on the approximate constancy of the differences in the atomic weights of elements forming a group, the ever-dominant desire for simplicity in numerical relations asserted itself. This led to unjustifiable attempts to alter the experimental values in order to make them agree with preconceived ideas. We know how variable and arbitrary were the criteria (prior to 1860) used in the determination of equivalent and atomic weights in general; but in the special cases of groups of elements there was more uniformity, hence the numbers obtained were comparable, and since the above considerations concerning classification applied only to groups of elements, it was possible to bring out within this compass a relation between atomic weight and properties. The extension to the case of elements in general soon followed. This was done in a set of short papers published from 1863 onward by Newlands, the forerunner of Lothar Meyer and Mendeleeff."

The work of Newlands followed immediately upon that of de Chancourtois, who was the first to devise a symmetrical arrangement of the elements in his theory of the "Telluric Screw." His first paper (1863) considered some numerical relations between the atomic weights. To quote from Venable's 'Periodic Law': "These relations were in part along the line of the old triads. Thus zinc was pointed out as the mean between magnesium and cadmium, copper between cobalt and zinc. In the group of the alkalies, one of lithium and one of potassium made two of sodium; one of lithium and two of potassium made one of rubidium, etc. Similar relations were observed for other groups. He also endeavored to show a certain kind of symmetry when the lowest member of a group was subtracted from the next higher member and when the lowest member of a triad was deducted from the highest."

In a paper published in 1864, Newlands furnished a table containing the elements arranged in the order of their

atomic weights. In a side column the differences between these weights were given, each being deducted from the one next higher in the scale. The next year Newlands announced his "law of octaves," which he deduced from his arrangement of the elements. He said in part that, "If the elements are arranged in the order of their equivalents, with a few slight transpositions, as in the accompanying table, it will be observed that elements belonging to the same group usually appear on the same horizontal line.

No.	No.	No.	No.	No.	No.	No.	No.	No.
H 1	F 8	Cl 15	Co 22	Br 29	Pd 36	I 42	Pt 50	
Li 2	Na 9	K 16	Ni 23	Rb 30	Ag 37	Cs 44	Ir 53	
B 3	Mg 10	Ca 17	Zn 25	Sr 31	Cd 38	Ba 45	Pb 54	
Bo 4	Al 11	Cr 19	V 24	Ce 32	U 40	Ta 46	Th 56	
C 5	Si 12	Ti 18	In 26	Zr 33	Sn 39	W 47	Hg 52	
N 6	P 13	Mn 20	As 27	Di 34	Sb 41	Nb 48	Bi 55	
O 7	S 14	Fe 21	Se 28	Ro 35	Te 43	Au 49	Os 51	

"It will also be seen that the numbers of analogous elements generally differ either by 7 or by some multiple of 7; in other words, members of the same group stand to each other in the same relation as the extremities of one or more octaves in music."

The same year he gave as an explanation of the existence of triads the fact that "in conformity with the Law of Octaves, elements belonging to the same group generally have numbers differing by seven or by some multiple of seven. That is to say, if we begin with the lowest member of a group, calling it 1, the succeeding members will have the numbers 8, 15, 22, 29, etc., respectively. But 8 is the mean between 1 and 15; 15 is the mean between 8 and 22, etc., and therefore as an arithmetical result of the Law of Octaves the number of an element is often the exact mean of those of two others belonging to the same group and consequently its equivalent also approximates to the mean of their equivalents."

Two years before the presentation of Newland's paper before the London Chemical Society, containing the "Law

of Octaves," Lothar Meyer (1830-1895), published the first edition of his 'Die Modernen Theorien der Chemie,' in which he gave a table of the elements arranged horizontally according to their atomic weights, so that analogous elements stood under one another and the change of valence, along with that of atomic weight, could be easily observed.

This was Meyer's first attempt, and his table exhibited less evidence of periodicity than that of Newlands, but it caused Meyer to give the question of the relationship of the atomic weights more serious consideration and his mind continued working on the atomic relationship. His first table had been in the following form:

MEYER'S FIRST TABLE. 1864.					
4 val.	3 val.	2 val.	1 val.	1 val.	2 val.
Diff. ....	....	....	....	Li 7.03	(Be 9.3)
C 12.0	N 14.4	O 16.00	F 19.0	16.02	(14.7)
Diff. 16.5	16.06	16.07	16.46	Na 23.5	Mg 24.0
Si 28.5	P 31.0	S 32.0	Cl 35.46	16.08	16.0
Diff. $\frac{1}{2}$ 44.45	44.0	46.7	44.51	K 39.13	Ca 40.0
....	As 75.0	Se 78.8	Br 79.97	46.3	47.0
Diff. $\frac{1}{2}$ 44.55	45.6	49.5	46.8	Rb 85.4	Sr 87.0
Sn 117.6	Sb 120.6	Te 128.3	I 126.8	47.6	49.0
Diff. $\frac{1}{2}$ 44.7	$\frac{1}{2}$ 43.7	....	....	35.5	
Pb 207.0	Bi 208.0	....	....	(Tl 204.0?)	Ba 137.1
4 val.	4 val.	4 val.	2 val.	1 val.	
{ Mn 55.1	Ni 58.7	Co 58.7	Zu 65.0	Cu 63.5	
{ Fe 56.0					
Diff { 49.2					
48.3	45.6	47.3	46.9	44.4	
Ru 104.3	Rh 104.3	Pd 106.0	Cd 111.9	Ag 107.94	
Diff. $\frac{1}{2}$ 46.0	$\frac{1}{2}$ 46.4	$\frac{1}{2}$ 46.5	$\frac{1}{2}$ 44.5	$\frac{1}{2}$ 44.4	
Pt 197.1	Ir 197.1	Os 199.0	Hg 200.2	Au 196.7	

On leaving Eberswald in 1868, he left with his successor the following elaborate table, according to Seubert:

SUGGESTION FOR A SYSTEM OF ELEMENTS BY LOTHAR MEYER. SUMMER 1868.

1	2	3	4	5	6	7	8
Cr = 52.6	Mn = 55.1 49.2 Ru = 104.3 92.8 = 2.46.4 Pt = 197.1	Al = 27.3 31.2 = 14.8 Fe = 56.0 48.9 Rh = 103.4 92.8 = 2.46.4 Ir = 197.1	Al = 27.3 Co = 58.7 47.8 Pd = 106.0 93 = 2.405 Os = 199	Ni = 58.7	Cu = 63.5 44.4 Ag = 107.9 88.8 = 2.44.4 Au = 196.7	Zn = 65.0 46.9 Cd = 111.9 83.3 = 2.44.5 Hg = 200.2	C = 12.00 16.5 Si = 28.5 32.1 = 44.5 33.1 = 44.5 Sn = 117.6 89.4 = 2.41.7 Pb = 207.0
9	10	11	12	13	14	15	
N = 14.4 16.96 P = 31.0 44.0 As = 75.0 48.6 Sb = 120.6 87.4 = 2.43.7 Bi = 208.0	O = 16.00 16.07 S = 32.07 46.7 Se = 78.8 49.5 118 = 128.3	F = 19.0 16.46 Cl = 35.46 44.5 Br = 79.9 46.8 I = 126.8	Li = 7.01 16.02 Na = 23.05 16.08 K = 39.13 46.3 Rb = 85.4 47.6 Cs = 133.0 71 = 2.35.5 Te = 203.0	Be = 9.3 14.7 Mg = 24.0 16.0 Ca = 40.0 47.6 Sr = 87.6 49.5 Ba = 137.1	Ti = 48 42.0 Zr = 90.0 47.6 Ta = 137.6	Mo = 92.0 45.0 V = 137.0 47.0 W = 184.0	



The following year Dmitri Mendeléeff (1834-1907), a Russian chemist, published his first paper embracing the important principles of the Periodic Law. He states that he was led to the consideration of the question in this way:

"When I undertook to write the text-book, entitled 'The Foundations of Chemistry,' I had to decide for some one system, lest, in the classification of the elements, I should have allowed myself to be guided by accidental, and, so to speak, instinctive reasons rather than by an accurate and definite principle."

Mendeléeff then showed that the principles hitherto used in classification had not been of a quantitative nature, and he laid stress on the superiority of a system which is based on numerical relations and therefore leaves no scope for arbitrary interpretation. Consideration of the numerical data available in the case of the elements led him to the rejection of the optical, electrical and magnetic properties, because these vary with the conditions; and of the vapor density, because this is not known for many elements, and is different for the allotropic modifications.

He next emphasized the unalterability of the atomic weight, stating that, "For this reason I have tried to take as basis for my system of classification the value of the atomic weight. . . . Beginning with the one of smallest atomic weight, I arranged the elements according to the magnitude of their atomic weights, when it became evident that there exists a kind of periodicity in the properties of the simple substances. . . ."

"Hence in this system of classification the atomic weight of an element determines the place to be assigned to it, . . . and all the comparative investigations that I have made lead me to the conclusion that the magnitude of its atomic weight determines the character of an element in the same measure, as the molecular weight determines the properties and many of the reactions of a compound.





MENDELÉEFF'S TABLE I.

Order No.	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII
	$R_2O$	RO	$R_2O_3$	$RH_2$ $RO_2$	$RH_3$ $R_2O_5$	$RH_2$ $RO_3$	$RH$ $R_2O_7$	
1	H = 1							$RO_2$
2	Li = 7	Be = 9.4	B = 11	C = 12	N = 14	O = 16	F = 19	
3	Na = 23	Mg = 24	Al = 27.3	Si = 28	P = 31	S = 32	Cl = 35.5	
4	K = 39	Ca = 40	— = 44	Ti = 48	V = 51	Cr = 52	Mn = 55	Fe = 56, Co = 59, Ni = 59, Cu = 63
5	(Cu = 63)	Zn = 65	— = 68	— = 72	As = 75	Se = 78	Br = 80	
6	Rb = 85	Sr = 87	? Yt = 88	Zr = 90	Nb = 94	Mo = 96	— = 100	Ru = 104, Rh = 104, Pd = 106, Ag = 108
7	(Ag = 108)	Cd = 112	In = 113	Sn = 118	Sb = 122	Te = 125	I = 127	
8	Cs = 133	Ba = 137	? Di = 138	? Ce = 140	—	—	—	
9	(—)	—	—	—	—	—	—	
10	—	—	? Er = 178	La = 180	Ta = 182	W = 184	—	Os = 195, Ir = 197, Pt = 198, Au = 199
11	(Au = 199)	Hg = 200	Tl = 204	Pb = 207	Bi = 208	—	—	
12	—	—	—	Th = 231	—	U = 240	—	

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MENDELÉEFF'S TABLE II.

Gr. Ser.	2.	4.	6.	8.	10.	12.
I.	Li 7	K 39	Rb 85	Cs 133	10	....
II.	Be 9.2	Ca 40	Sr 87	Ba 137	....	....
III.	B 11	? Sc	Yt 89?	Di 139?	Er 175?	....
IV.	C 12	Ti 48	Zr 90	Ce 141	La 180?	Th 231
V.	N 14	V 51	Nb 94	? 2	Ta 182	....
VI.	O 16	Cr 52.5	Mo 96	? 2	W 184	Ur 240
VII.	F 19	Mn 55	....	..	....	....
VIII.		Fe 56	Ru 103	..	Os 194	....
		Co 58.6	Rh 104	..	Ir 195	....
		Ni 58.6	Pd 106	..	Pt 197	....
I.	H 1	Na 23	Cu 63.5	Ag 108	..	Au 197
II.		Mg 24	Zn 65	Cd 112	3	Hg 200
III.		Al 27.3	Ga 69	In 113	..	Tl 204
IV.		Si 28	??	Sn 118	..	Pb 204
V.		P 31	As 75	Sb 120	..	Bi 208
VI.		S 32	Se 79	Te 125?	..	....
VII.		Cl 35.5	Br 80	I 127	..	....

These tables contain the Periodic Law as it is known to us. They have not been very materially altered, tho they have been corrected in minor points. The work since has been mainly one of elaboration, and, as Venable observes, "The credit for the expansion and filling out of the Periodic Law, its extension to the other properties of the elements and the bringing of the various compounds of these elements into consideration also, has been almost entirely due to the skill and knowledge of Mendeléeff."

In 1870, Meyer offered a full table representing the nature of the elements as a function of their atomic weights which was so similar to Mendeléeff's that many accused him of plagiarism, but his claims to the authorship of the Periodic Law are based on his 1864 and 1868 tables, and his 1870 system appears to have been an expansion of his earlier tables. It is generally considered that Mendeléeff and Meyer worked out the Periodic Law independently.

LOTHAR MEYER'S TABLE REPRESENTING THE NATURE OF THE ELEMENTS AS A FUNCTION OF  
THEIR ATOMIC WEIGHTS

I	II	III	IV	V	VI	VII	VIII	IX
	B = 11.0	Al = 27.3		—	—	? In = 113.4	—	Tl = 202.7
	C = 11.97	Si = 28	Ti = 48	—	Zr = 89.7	Sn = 117.8	—	Pb = 206.4
	N = 14.01	P = 30.9	V = 51.2	As = 74.9	Nb = 93.7	Sb = 122.1	—	Bi = 207.5
—	O = 15.96	S = 31.98	Cr = 52.4	Se = 78	Mo = 95.6	Te = 128 ?	Ta = 182.2	—
	F = 19.1	Cl = 35.38	Mn = 54.8	Br = 79.75	Ru = 103.5	I = 126.5	W = 183.5	—
			Fe = 55.9		Rh = 104.1		Os = 198.6 ?	
			Co, Ni = 58.6		Pd = 106.2		Ir = 196.7	
Li = 7.01	Na = 22.99	K = 39.04		Rb = 85.2	Ag = 107.66	Cs = 132.7	Pt = 196.7	—
? Be = 9.3	Mg = 23.9	Ca = 39.9	Cu = 63.3	Sr = 87.0		Ba = 136.8	Au = 196.2	—
			Zn = 64.9		Cd = 111.6		Hg = 199.8	—

Difference from I to II and from II to III about = 16.  
Difference from III to V, IV to VI, V to VII fluctuating about 46.  
Difference from VI to VIII, from VII to IX = 88 to 92.

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The Periodic Law soon attracted merited attention, but for several years its importance was not generally recognized, and it was not until the discovery of some new chemical elements, thereby fulfilling certain predictions of Mendeléeff, that it became accepted.

Mendeléeff had obtained the atomic weights of elements not fully investigated by taking the mean of the weights of what he termed the "atom-analogues." For instance, the atom-analogues of selenium were arsenic and bromine on the one hand, sulphur and tellurium on the other; its

$$\text{atomic weight should be } \left\{ \frac{75 + 80 + 32 + 125}{4} \right\} = 78.$$

He had also applied the Periodic Law to the determination of the properties of unknown elements. This was accomplished by estimating the physical and chemical character from those of the atom-analogues, since he had established that all properties were functions of atomic weight. He described the properties of three undiscovered elements, and the following values he predicted will show why the Periodic Law was finally gladly accepted:

### EKA-ALUMINIUM

Suggested by Mendeléeff

Atomic weight, 68.

Specific weight, 60.

Atomic volume, 11.5.

### GALLIUM

Discovered in 1875 by Lecoq de  
Boisbaudran

Atomic weight, 69.9.

Specific weight, 5.96.

Atomic volume, 11.7.

The other, eka-silicon ( $Es = 72$ ), was discovered by Winkler in 1886. It is now called germanium ( $Ge = 72$ ).

At the present time all chemists recognize the dependence of the properties of the elements upon the atomic weights, and the periodic law has become the central idea in the classification and study of the elements and their compounds. This law is the greatest discovery in chemistry since the announcement of Dalton's atomic theory, and has been much more rapidly accepted. It promises to lead up to results of the utmost importance.

The close and mystifying relationship existing between the chemical elements which was revealed by the Periodic Law, naturally has attracted the minds of scientists to thoughts similar to the conception of one primordial matter as expressed by the Ionian philosophers, and later by Bacon, Descartes and Boyle. To quote Freund:

"Within the last two decades experimental evidence, physical and chemical, has been accumulating in support of these speculations, and the last few years' contributions have been such as to make the complexity of the atoms as much of an established fact as that of the molecular and atomic structure of the masses of matter that we perceive. Moreover, the empirical results which, taken in their entirety, can almost be said to have proved this point, have also supplied evidence which justifies the course hitherto followed by chemists in assigning to the atoms a very special place in the scale of the complexity of different kinds of matter. It seems that the diversity of matter begins only with the atom: that while the component parts of a molecule A are not the same as those of another kind of molecule B, or C, or D, etc., the constituents of an atom M are identical with those of any other different atom P, or Q, or R, etc.; that all atoms are compounded of the same one kind of primordial matter."

The most important papers which have been published on the unity of matter and on the composite character of the

elements are those of Sir William Crookes, Anton Grunwald, Gustav Wendt, Henry Wilde, Eduard Meusel, W. Preyer, C. T. Blanshard and Sir Norman Lockyer.

Of these speculations and views, the most important is the hypothesis of Crookes. According to him, the chemical elements have resulted by gradual condensation from a primary material which he terms "protyle." He arrived at this view in 1886 from observations on the phosphorescence spectra of the yttrium earths. When he advanced this hypothesis, "provisionally," Crookes had to assume the complexity of the elementary atoms, but since then experimental and theoretical knowledge on this point has become more definite, as is shown by J. J. Thomson's investigations on the structure of the atom. Thomson started from the hypothesis that the atom is an aggregation of a number of simpler systems, and that these are formed by "corpuscles" associated with equal charges of positive electricity. He then traced the analogies between atomic structures and atomic properties, and furnished an explanation for the empirical relations between atomic weight and atomic properties embodied in the Periodic Law. As Freund remarks, "In a section of the community usually referred to as the 'general public' there seems to be an impression that the recognition of the divisibility of the atom has dealt a deathblow to that atomic theory which was founded by Dalton just a hundred years ago. No misconception could be more complete. While nothing has had to be given up, nothing to be modified, there has been deepening of the foundations, extension of scope, correlation with other sciences. Except that some of the anticipations expressed have since been realized, the situation to-day is what it was when Kekulé" stated that while from a philosophical standpoint he did not believe in the actual existence of atoms, yet as a chemist he regarded the assumption of atoms, "not only as advisable, but as absolutely necessary in chemistry."

## CHAPTER XVI

### THE DEVELOPMENT OF APPLIED CHEMISTRY

ANALYTICAL chemistry—that division of chemistry which treats of the methods of ascertaining the chemical composition of substances and mixtures both as to kind (qualitative analysis) and quantity (quantitative analysis)—has been an indispensable aid to all branches of chemistry, pure and applied, during their modern development, and has itself undergone considerable elaboration and perfection. In particular, analytical methods, both qualitative and quantitative, have been and are being continuously improved.

The services of Boyle, Hoffmann, Marggraf, Scheele and Bergman in qualitative analysis have been mentioned, and it will be remembered that Bergman was the first to publish a system of qualitative analysis in the wet way. He laid a firm foundation for the methodical employment of reagents, and the methods of qualitative analysis now in use have been developed from his analytical course of procedure. Wilhelm August Lampadius and Johann Göttling contributed materially to the systematic arrangement of the analytical methods in use during the first decade. The former published in 1801 his "*Handbuch der Chemischen Analyse der Mineralkörper*," and the latter his "*Praktische Anleitung zur Prüfenden und Zerlegenden Chemie*" in 1802. Other works followed these, and analytical methods became known and improved.

Qualitative analysis in the dry way has been perfected



by the use of the blowpipe, an instrument which was originally employed for soldering metals, and which was first employed for testing minerals by Cronstedt and Engeström. Bergman and Gahn studied thoroly the deportment of various substances and reagents under the flame of the blowpipe, and their treatise on this important branch of chemical analysis was published in 1779. Berzelius, Hausmann and Wollaston later became interested in this field, and Berzelius, who was notably instrumental in introducing the blowpipe into chemistry, published a treatise on the application of this instrument in 1820. More recently the art of dry assay ("docimacy") was considerably advanced by the important flame-reactions of Bunsen. His treatise, "Flammen-Reactionen," was published in 1880.

After the preparatory investigations of Bergman, Klaproth, Vauquelin and Proust, it was Berzelius who worked out new methods of quantitative analysis, thereby promoting the systematic development of this branch. He had shown great ingenuity and inspired his pupils, more especially Heinrich Rose and Friedrich Wöhler, with like powers. Rose and Wöhler extended the observations of Berzelius, and made analytical methods generally known by the publication of their treatises. The "Handbuch der Analytischen Chemie" of the former first appeared in 1829, and passed through six German editions and three French editions; while the "Practische Uebungen in der Chemischen Analyse" of Wöhler, which was published in 1853, was translated into Russian, French

tion of his "Anleitung zur Qualitativen Chemischen Analyse" in 1841 and his "Anleitung zur Quantitativen Chemischen Analyse" in 1846. These works have been published in numerous editions and translations since.

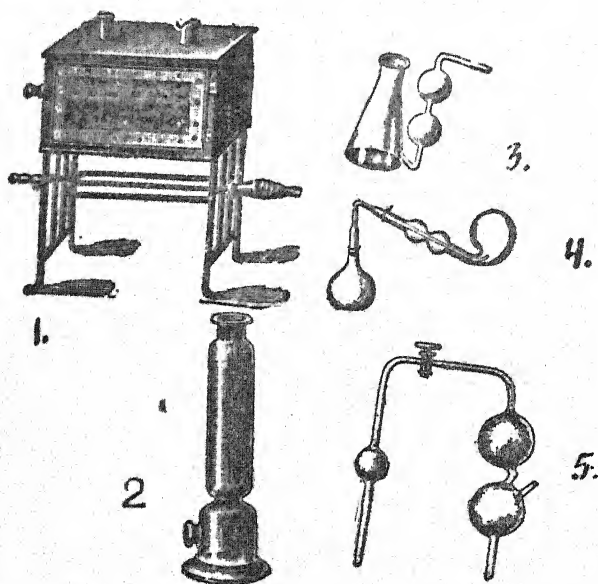


Fig. 30 —APPARATUS DESIGNED BY FRESERIUS.

1., hot-air oven; 2., gas-drying jar; 3., absorption flask; 4., chlorine distillation apparatus; 5., distillation head.

Other chemists who have aided in the discovery of new tests, improved methods of separation and determination, and in the designing of suitable chemical apparatus for analytical operations are Liebig, Stromeyer, Bunsen, Fremy, Turner, Scheerer, Rammelsberg, Gibbs, Blom-

strand, Marignac and Winkler. Classen's services in electro-analysis are noteworthy.

Volumetric analysis—that process in which the reagents are employed in solutions of known strength—has been greatly developed during the last seventy years, and volumetric methods are much used in technical analysis, owing to the fact that no weighing is necessary after the standard solutions are once made up, thus saving considerable time.

The quantitative analysis of gases was greatly perfected by Bunsen, whose researches in this direction began in 1838. Bunsen published methods of estimating various gases by absorption and combustion, which have required only slight modifications since, but the qualitative analysis of gases has only lately been developed in a scientific manner. The work of Winkler in this connection has been important, and he and Hempel have improved the apparatus for gasometry and gas analysis and have generalized methods.

The quantitative analysis of organic compounds has gradually developed from the observation that carbonic acid and water are products of their combustion. Lavoisier indicated the right path here, and his process was improved upon by Gay-Lussac and Thénard, Berzelius, Liebig, and more recently by Dennstedt, Collie and Hempel. The exact determination of nitrogen only became possible after 1830, when Dumas had devised his method. Other methods of determining nitrogen have been worked out by Will and Varrentrapp, and by Kjeldahl, whose method is extensively used in agricultural-chemical analysis for estimating protein. Many methods for determining the halogens, sulphur, phosphorus, and other elements which occur less frequently in organic bodies, have been worked out, and these have found extended application in forensic chemistry, hygiene and agricultural chemistry.

The beginnings of phytochemistry, the chemistry of plant-life, can be traced back to investigations made at the close of the eighteenth century.

Priestley, Senebier, de Saussure, and others were familiar with the fact that green plants under the influence of sunlight will remove carbonic acid gas from the atmosphere and decompose it. They were also aware of the fact that ammonia salts are of value in stimulating the growth of plants, Nicolas Leblanc having pointed this out at the end of the eighteenth century.

Altho the problems of plant-life, the mode and manner of plant-nourishment and growth, had engaged the labors of many trained observers for many years, yet even during the first three decades of this century the belief was almost universal that plants, like animals, derived their nourishment directly from organic matter.

This assumption found its chief advocates in Germany and France in Albrecht Thaer and Mathieu de Dombasle respectively. In their opinion inorganic salts, the importance of which could not be absolutely denied, acted merely as stimulants and not as if they were essential to the growth of the plant. Indeed, Thaer held that the creation of earths in plants through their vital forces was possible. In this assumption he followed the opinion of Schrader, who so early as the year 1800 imagined that he had proved by actual experiments the generation of the ash-constituents of plants by the vital forces.

J. G. Wallerius, a Stockholm chemist, had sought to lay a much more rational foundation for agricultural chemistry in 1761 in his "*Akerbrukets Chemiska Grunder*," when he made a comparison between the plant constituents and the constituents of the soil on which they grew.

It was Justus von Liebig who demonstrated the falsity of the views of Thaer and Dombasle, and who entirely disproved the humus-doctrine, as the theory held at that time was called. It was in 1840, after exhaustive investigations on the weathering of rocks, on the formation of soils, and on the effects of rain and the gases which rain holds in solution, that Liebig published his classic work on the application of chemistry to agriculture and physiology.

In this Liebig completely undermined the foundations of the humus theory and enunciated the following foundation principles of modern agricultural chemistry:

1. Inorganic substances form the nutritive material for all plants.

2. Plants live upon carbonic acid, ammonia (nitric acid), water, phosphoric acid, sulphuric acid, silicic acid, lime, magnesia, potash and iron; many need common salt.

3. Manure, the dung of animals, acts not through the organic elements directly upon plant-life, but indirectly through the products of the decay and fermentative processes; thus carbon becomes carbonic acid and nitrogen becomes ammonia or nitric acid. The organic manures, which consist of parts of remains of plants and animals, can be substituted by the inorganic constituents into which they would be resolved in the soil.

Practical field trials, carried out by governments and large land-owners, proved the correctness of Liebig's deductions from his laboratory experiments, and the many investigators in this line since have come either directly or indirectly from Liebig's school. Liebig's conclusion that one must restore to the soil that which the removal of the crop had withdrawn, if one would prevent its exhaustion, is the basis of successful agricultural practice to-day.

A French chemist, J. B. Boussingault, worked independently along similar lines to Liebig, and the services which he rendered in carrying out researches on the nutrition of plants by new methods were of great importance.

Mention may be made here about nitrification in soils and the assimilation of free nitrogen by plants, the most important discoveries in agricultural chemistry of recent years. In 1849, Georges Ville, then director of the Agricultural Experiment Station at Vincennes, proved by actual experiment that certain plants assimilate free atmospheric nitrogen, but his conclusions were strongly disputed, being directly opposed to those of Boussingault and Liebig, and also to subsequent investigations by Lawes,

Gilbert and Pugh in 1857. An important experiment bearing on the point and extending over many years was begun in 1855 by Herr Schultz, of Lupitz, in Altmark, Germany. He grew lupines on very poor soil with the addition of non-nitrogenous manures only and found that, notwithstanding this, the soil became richer in nitrogen year by year. The next step toward the solution of the question was the discovery in 1877 of the now well-known process of "nitrification" in soils by Schloesing and Müntz, this nitrification being the work of definite microbes, some of which have been isolated, while more recent work has proved that the direct assimilation of atmospheric nitrogen by leguminous plants is brought about by the agency of certain micro-organisms (tubercle bacteria) originally present in the soil. Cultures of these specific bacteria are now prepared on a manufacturing scale, under the name of "nitragins," for application to soils naturally deficient in them.

It only remains to mention as a factor in the present and future growth of agricultural chemistry the experiment stations and laboratories established now by the governments of every civilized country. In the United States, for example, there are at present sixty-one agricultural experiment stations, all in charge of efficient specialists, and many intricate problems of national importance have been solved.

The large chemical industries and, in fact, all branches of chemical technology have been immensely developed during the nineteenth and twentieth centuries, and the achievements of chemistry in the arts and industries have been stupendous and varied.

During the Modern Chemical Period pure chemistry and applied chemistry have been constantly interactive, and the latter has profited immensely by the extension of the former, while pure chemistry (theoretical, inorganic, organic and practical chemistry) has in turn been greatly



benefited by the opportunities offered by the industries. The advancement of technical chemistry has been especially aided, however, by the development of analytical chemistry, which has allowed of a keen insight into the composition of the various industrial products, thereby leading to the introduction of many technological innovations. Then, too, industrial research has been and is being constantly fostered by chemical manufacturers, and this has led to the accruelement of important novelties and improvements.

The literature of technical chemistry is very extensive, but the standard treatises of Rudolf von Wagner ("Handbuch der Chemischen Technologie"), Karl Karmarsch ("Geschichte der Technologie seit der Mitte des achtzehnten Jahrhunderts"), T. E. Thorpe ("A Dictionary of Applied Chemistry") and Ernst von Meyer ("A History of Chemistry," translated by McGowan) contain accounts of the development of the important industries.

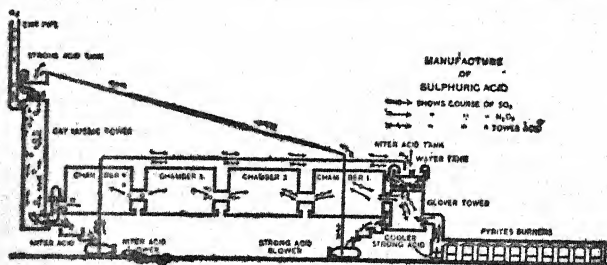
The manufactures of sulphuric acid and soda, which may be looked upon as the basis of all the other chemical industries and which are naturally followed by those of hydrochloric acid, bleaching powder, chlorate of potash, and other salts of potassium, nitric acid, etc., only attained to their full vigor after the various processes involved had been explained by chemical investigation and after the most favorable conditions for those processes had been worked out.

Important practical improvements were made in the manufacture of sulphuric acid so early as the beginning of the nineteenth century—*e.g.*, the amount of steam required was regulated and the process was made continuous (the latter by Holker). The first attempt to explain this remarkable chemical process of the formation of sulphuric acid from sulphurous acid, air, water and nitrous gas was made by Clément and Désormes, who recognized the important part played by the nitric oxide. How essential for the manufacture the careful observations on the chemi-



cal behavior of nitrous acid to sulphurous and sulphuric have been is sufficiently evidenced by the introduction of the Gay-Lussac and Glover towers to which they gave rise and which have made the process into one complete whole.

In 1831, Peregrine Phillips discovered the "contact process" by bringing about the combination of sulphur dioxide and oxygen in presence of platinum, but it was only forty to fifty years later that Clemens Winkler converted this experiment into a technical manufacture. The contact process, in many modifications, has developed and



improved so rapidly that many think it will eventually supplant the old chamber process altogether.

Common salt forms the foundation of the soda industry, whose history commences with the beginning of the modern chemical period. Nicolas Leblanc was the first to succeed in converting salt into soda, with sodic sulphate as an intermediate product, Malherbe and de la Metherie having some time previously attempted to utilize the latter substance in the same way, but without material success. It was in 1791 that Leblanc commenced the actual manufacture of soda, and in the year 1823 Muspratt began the erection of his alkali works at Liverpool; his name deserves a foremost place in connection with the development of the soda industry. The formation of soda from

the sulphate, by fusing the latter with coal and limestone, was ultimately so far explained by exact chemical experiments as to allow of a tenable theory of this fusion process being advanced.

Scientific researches have also given rise to numerous important improvements in the soda manufacture—e.g., to the beautiful process of Hargreaves and Robinson, by which sulphate of soda is prepared directly without the previous production of sulphuric acid, to the introduction of revolving soda furnaces, and to many processes for utilizing and rendering harmless the unpleasant alkali waste. But the greatest advance of all in this direction is the comparatively recent and exceedingly simple process of Chance, by which nearly all the sulphur in alkali waste can be recovered at a very cheap rate.

Purely chemical observations have also led to what was, until quite recently, the most important of all the innovations in the soda industry, viz., the conversion of common salt into carbonate of soda without the intermediate formation of sulphate at all, by the ammonia-soda process. The manufacture of "ammonia soda" and of artificial manures has grown so enormously of late years that the demand for salts of ammonia has increased proportionately, but this requirement has in its turn been met by the introduction of improved apparatus for the working up of gas liquor and by the successful attempts to extract the nitrogen of fuel in the form of ammonia, at the same time that the heat from the fuel or the residual coke is itself being utilized.

Berthollet's experiments upon the bleaching action of chlorine and the chlorides of the alkalies led to the manufacture of the bleach liquor known under the name of "Eau de Javelle." Chloride of lime was first produced by Messrs. Tennant & Co. in Glasgow in the year 1779. Weldon's process for the recovery of the manganese dioxide, required in the preparation of chlorine, from the otherwise worthless chlorine waste has been in practical working

since 1867. Deacon's method of producing chlorine directly from hydrochloric acid has never been very widely used.

The manufacture of bromine and iodine is based upon the original work of Gay-Lussac and Balard. Laboratory experiments have also led to the production of iodine from mother liquors which were formerly looked upon as valueless—e.g., those from Chili saltpeter and from phosphorite after its treatment with acid. To A. Frank is due the merit of having made bromine available for technical purposes by preparing it from the mother liquor of the Stassfurt waste salts.

Nitric acid plays an important part in chemical industries, especially since the development of the manufacture of explosives on a large scale. Potassium nitrate, which has been known and valued for so long, is still an indispensable ingredient of black gunpowder. Since the introduction of the nitrate of soda from the Chili deposits, nitric acid has been prepared from it (instead of from the more expensive nitrate of potash) by the old process of distillation with sulphuric acid, the latest advance here being the distillation of the nitric acid in a vacuum.

The explosives, whose preparation now forms a great industry, have all been made available for practical use by chemical investigations. The epoch-making discovery of gun-cotton by Schönbein and Böttger (independently) in 1846 must be recalled here. Nitro-glycerine had been known as a chemical preparation, discovered by Sobrero, for fifteen years before it began to find extended application in 1862, as the result of Nobel's researches.

The match industry owes its enormous development to the increased knowledge of chemical preparations and processes. There is a marked contrast between the "chemical tinder" of 1807—i.e., matches containing a mixture of chlorate of potash and sulphur, which were ignited by dipping them into sulphuric acid—and the present friction matches! Those prepared with ordinary yellow phos-

phorus were most probably first introduced in 1833 by Irinyi of Pesth, and subsequently by Romer of Vienna and Moldenhauer of Darmstadt; they have since undergone many improvements, the most important of these being subsequent to the discovery of amorphous (non-poisonous) phosphorus, which has been used since the year 1848. Phosphorus has been manufactured on the large scale for about fifty years. Scheele's process for its preparation was improved upon by Nicolas so far back as 1778, and has been materially modified in recent years.

Closely connected also with the soda industry are the manufactures of ultramarine and of glass. The former substance was discovered in 1828 by Chr. Gmelin and at about the same time by Guimet; a little later it was also discovered, independently, by Köttig of Meissen, who was the first to prepare it on a technical scale.

The production of glass reached a high state of development in olden times through pure empiricism, but has greatly benefited by chemical research. The manufacture of glass with sulphate of soda, and the improvements in flint and crystal glasses belong to the last century, while progress has also been made in silvering (by Liebig), and in glass painting through the discovery of new mineral colors.

Water glass, which was known to Agricola and Glauber, was made available for technical purposes by Fuchs in 1818, and has since then been used for a great number of different purposes—*e.g.*, for impregnating wood and preparing cements.

The attempts to utilize raw vegetable products, particularly wood and straw, for the production of paper were first carried out in the year 1846. In caustic soda a reagent was found by means of which cellulose could be prepared from these materials, while of late years a solution of calcium sulphite in sulphurous acid has shown itself especially well adapted for this purpose. The above process for the production of sulphite cellulose resulted from the chemical

investigations of Tilghman. Cross and Bevan's discovery that cellulose can be dissolved by carbon disulphide and soda, and thus be converted into a soluble cellulose xanthate has enormously extended the uses to which the plastic material can be put. Objects of all kinds, from

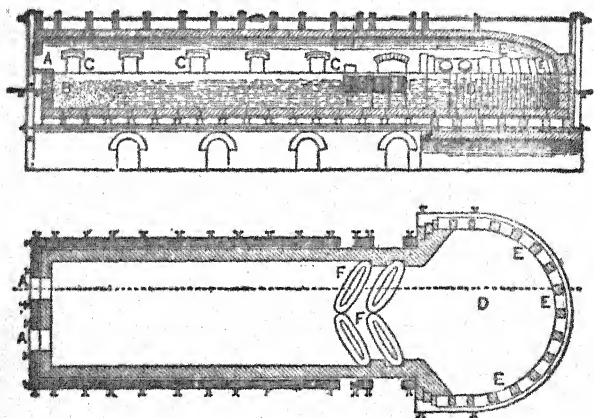


Fig. 31 —GLASS TANK-FURNACE.

Plan and elevation of a tank-furnace for the manufacture of glass. The batch is introduced at (A.), and a gas flame issues from (C, C.) and plays over the surface of the charge. The batch (B.) soon fuses and the liquid mass flows toward the opposite end of the tank. At (F.) are elliptical "floaters" of fire-clay, one end of which rests in recesses in the wall, while the free ends meet in the middle of the furnace. The current of melted glass, flowing toward (D.), constantly presses these floaters together and prevents their separation. The liquid mass thus passes under the "floaters" and collects in the compartment (D.), from which it is withdrawn through the openings (E., E.).

"artificial silk" to billiard balls, can now be made of pure cellulose.

The beet-sugar industry has developed into an enormous manufacture from experiments carried out by chemists on a small scale. Marggraf's discovery, in 1747, that sugar

was present in the juice of beet, was not at that time capable of being applied commercially. Achard, a pupil of Marggraf, and others again took up at the end of the eighteenth century the problem of obtaining sugar from beet on the large scale, and they devised a process which was carried out in factories during the years of the Napoleonic wars. However, this process was unable to exist, being a very imperfect one and giving but a small yield of sugar, and it is from the year 1825 that the real rise of the beet-sugar industry dates, various factors entering into its growth, not the least of which was the practical application of chemical knowledge. Scheibler's strontia process for obtaining the crystallizable sugar from molasses is based upon a knowledge of the various saccharates of strontia. The filtration of the refined juice through bone charcoal was first recommended by Figuier in 1811 and then by Derosne in 1812, and has since become an essential part of the process. The use of vacuum pans for evaporating the syrup was introduced by Howard in 1813, since which time many improvements have been made in them. Osmosis, which was first applied on the large scale by Dubrunfaut in 1863 for extracting the crystallizable sugar from molasses, was developed by researches in physical chemistry.

The development of the fermentation industries has been immensely extended by chemical investigation, while at the same time the nature of the processes themselves has been explained. The latest work of E. Buchner and his pupils has resulted in showing that fermentation is brought about by an enzyme ("zymase") produced from the yeast.

Among the more important observations in this branch during recent years are those of Effront upon the favorable effect of a minute quantity of hydrofluoric acid on the fermentation process, and of others upon the advantages gained by ventilation and by the use of pure yeast cultures.

A knowledge of the normal composition of wine and beer has led to rational suggestions for the improvement of those liquors. It would be impossible to attempt even a



bare enumeration of the more important innovations in this branch, many of which are due to Pasteur—*e.g.*, the Pasteurization of beer.

In no other section of technical chemistry have there been so many discoveries made by systematic investigation as in that of artificial dyes.

The first aniline dye which was produced upon a technical scale was the mauve prepared by W. H. Perkin in 1856, by acting upon aniline with bichromate of potash and sulphuric acid, and it is to him that the introduction of the color industry is due. A. W. Hofmann observed in 1858 the formation of aniline red (magenta), which was shortly afterward manufactured by another method by Verguin of Lyons and introduced into commerce under the name of fuchsine. This was followed by the discovery of aniline blue, aniline violet and aniline green, all of which were first prepared by Hofmann himself, while he proved that all of them were derivatives of fuchsine. The discovery of methyl violet by Lauth in 1861 and that of aniline black by Lightfoot in 1863 were of great practical importance. In addition to this new and important methods for the production of rosaniline dyes have been discovered and developed—*e.g.*, oxalic acid, formic aldehyde and carbonyl chloride are now used for the synthesis of diphenylamine blue, the new magenta, methyl violet, and allied compounds.

The valuable dye alizarine was formerly prepared entirely from the madder root, but is now obtained from coal-tar, this revolution having been brought about by Graebe and Liebermann's successful synthesis (in 1869) of alizarine from anthracene, a constituent of coal-tar. Following alizarine, other derivatives of anthracene were prepared from the year 1880 onward.

An immense industry—that of so-called chemical preparations—has gradually been developed on scientific lines from apparently insignificant beginnings which had their origin in the work of the apothecary; such "preparations" belong partly to inorganic and partly to organic chemistry.



As instances of this one may take the great increase in the production of silver salts, bromine and iodine for photographic and other purposes, and the manufacture of numberless other metallic salts—*e.g.*, thiosulphates, hydrosulphites, borates and silicates, not to speak of newly introduced compounds like the peroxides of hydrogen and sodium, sodium persulphate and other per-salts and compounds of lithium, rubidium, vanadium, etc. The already imposing list of inorganic preparations is being continually added to.

The manufacture of organic preparations is still more extensive. The various alcohols themselves, their ethers and esters, chloroform, chloral, iodoform, aldehyde, etc., are now all essential to chemical manufactures and to medicine. The processes by which these compounds are manufactured are the result of scientific researches, old and new.

From what has been said it is seen that coal-tar is the raw material from which many organic preparations are obtained, the technical importance of which it is difficult to estimate. Formerly a troublesome waste material, it is now of at least equal value with the other products from the distillation of coal. The manufacture of ammonia and salts of ammonia from gas liquor is now a thoroly rational one, thanks to the careful chemical examination of the latter, and it forms a large and important branch of industry.

The manufacture of coal gas was at first developed quite empirically, and it was only in the second half of the nineteenth century that improvements were introduced which were based upon the scientific investigation of the relations existing between the composition of the gas and the mode in which the distillation of the coal was conducted, and this also applies to improved methods of purifying the crude gas. The present distillation process was introduced about the year 1880, after it was seen that by raising the temperature of decomposition the yield of gas from pit

coal was nearly doubled. In order to achieve the necessary white heat, gas retorts are now made from the most refractory fireclay (instead of iron), and they are heated by regenerator gas.

About fifteen years ago acetylene began to come into prominence as an important illuminant; indeed, enthusiasts on the subject prophesied that the brilliant light which it gave would prove to be "the light of the future." Pro-

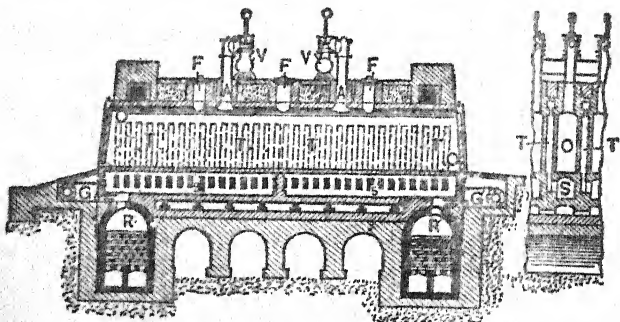


Fig. 32 —BY-PRODUCT COKING OVEN.

Plan of the Otto-Hoffmann by-product oven. In this type the retorts are narrow chambers (O.) about 40 feet long, 5 feet high and 22 inches wide, having doors at each end, and heated by vertical flues (T., T.) in the walls. Coal is charged through (F., F.), while the gases and tar pass off through (A., A.) to the hydraulic main (V., V.).

duced from calcium carbide, a product of electro-chemistry, it looked for a time as if acetylene were destined to become a formidable competitor of the electric light.

The first impulse toward the use of furnace gas as a heating agent was given by the experiments of Faber de Faur and of Bunsen, experiments made with the object of utilizing the gases issuing from the mouth of iron blast furnaces, which are rich in carbon monoxide. These, as well as the gases from coking ovens, were for long allowed

to escape, and still are to some extent, but for the most part they now constitute important sources of heat. Lowe introduced "water gas" into technical use in 1875, preparing it by passing steam over red-hot coal; it is now much used for heating and illuminating purposes and will undoubtedly become even more employed in time.

The above résumé of the development of industrial

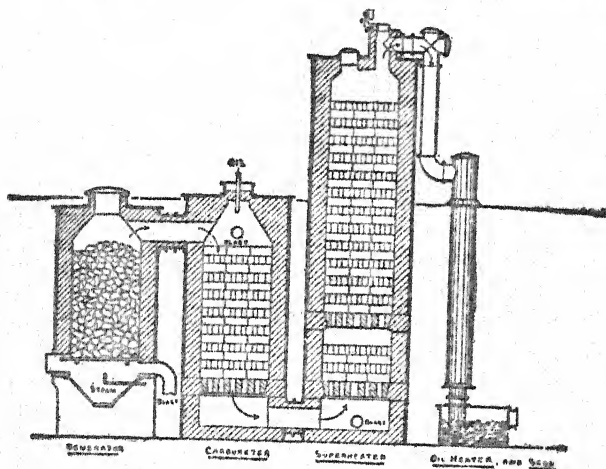


Fig. 33 —MANUFACTURE OF WATER GAS.

The Lowe process for making illuminating water gas.

chemistry during the Modern Period will indicate how it has been elevated by a continuous infusion of scientific spirit, and manufacturing, once a matter of empirical judgment and individual skill, is more and more becoming a system of scientific processes. Quantitative measurements are replacing guesswork, and thus waste is diminished and economy of production insured. In the United States several decades ago few industrial establishments furnished regular employment to chemists, but now American manu-

facturers are becoming more and more appreciative of scientific research, and the results so far obtained have resulted in far-reaching improvements. In the production of a metal from its ores, or of indigo from coal-tar, it is chemistry that points the way, and the more complex the problem the greater the dependence. In devising new processes and in the discovery of new and useful products, chemistry is again the pathfinder. The community is apt to overlook the extent and diversity of the services rendered by the chemist, because of the quiet and unobtrusive way in which the work is carried out.

The measure of a country's appreciation of the value of chemistry in its material development and the extent to which it utilizes this science in its industries, generally measure quite accurately the industrial progress and prosperity of that country. In no other country in the world has the value of chemistry to industry been so thoroly understood and appreciated as in Germany, and in no other country of similar size and natural endowment have such remarkable advances in industrial development been recorded, and this, too, with steadily increasing economy in the utilization of the natural resources.

Ex-President Roosevelt has well said, "The life of the nation depends absolutely on the material resources which have already made the nation great," and M. T. Bogert recently has eloquently indicated how the chemist can and will be of service in that great problem, the conservation of natural resources. This work is not entirely that of the engineer, and, with the awakening of the producer and manufacturer to the value of science in industry, the outcome of the conservation movement can only be a successful one through the assistance of the chemist.

